Cryoscopic Studies on the Transition Points of the Compounds of Organic Solvents with Salts. III. The Congruent Melting Points of some Alcoholates of Alkali Halides.

By Hazime OOSAKA.

(Received April 12th, 1937.)

In previous papers[1][2] certain transition points at which the solid solvate melted to form the anhydrous salt and a solution saturated with this salt were cryoscopically studied and it was shown that this temperature was lowered by the addition of foreign substances according to the following relation,

$$\Delta T = K \frac{100\,w}{WM}\,, \qquad (1)$$

where ΔT is the depression of the transition point, K the molecular depression referred to 100 g. of the pure solvent, w the weight of a foreign substance dissolved in W g. of the pure solvent and M the molecular weight of the foreign substance. The constant K referred to 100 g. of the pure solvent was preferred to that referred to 100 g. of the solvate corresponding to the experimental procedure.

In a number of systems there exists a congruent melting point at which a solid solvate melts completely and yields a liquid of the same composition as the crystalline solvate. This temperature may be also considered as a transition point for the alcoholate and its melt. The lowering of the congruent m. p. by the addition of foreign substances has been similarly investigated on the systems formed by alcohols and alkali halides: LiCl–CH_3OH, LiCl–C_2H_5OH, LiBr–C_2H_5OH, and LiBr–n-C_3H_7OH, and the results are given in the present communication.

The Solubilities of the Systems and the Congruent Melting Points. In the present systems the forms of the solubility curves exhibit a close parallelism to each other and the general type is shown by the diagrammatic curve in Fig. 1. The solubility curve of the alcoholate ABC possesses a retroflex region, represented in the figure by BC. The point B is the congruent m.p. The solubility of the anhydrous salt changes

(1) H. Oosaka, this Bulletin, **3** (1928), 289.
(2) H. Oosaka, *Sci. Repts. Tokyo Bunrika Daigaku*, A, **1** (1933), 241.

CHEMISTRY HALL LIBRARY

only slowly with temperature and its curve CD cuts the curve ABC at the point C. This point is the transition or eutectic point for the alcoholate and the anhydrous salt.

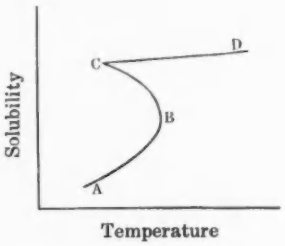


Fig. 1.

The system LiCl–CH_3OH. Simon[3] observed the existence of the solid alcoholate $LiCl \cdot 3CH_3OH$. The solubility curve of the anhydrous salt was determined by Lloyd, Brown, Bonnell and Jones,[4] and they described the transition point as 0.1°C. The solubility of the alcoholate had not been found so that the author made the preliminary determination and redetermined the solubility of the anhydrous salt.[5] The results showed that the congruent m.p. (B in Fig. 1.) coincided approximately with the transition point (C in Fig. 1.) and was 12.9°C.

The system LiCl–C_2H_5OH. The solubilities of the alcoholate $LiCl \cdot 4C_2H_5OH$ and the anhydrous salt were determined by Turner and Bissett,[6] the existence of the crystalline alcoholate being confirmed by them. Their solubility curve of the alcoholate possesses a retroflex portion, but they did not describe this behaviour. From their curve about 18°C. can be read as the congruent m.p. By the cryoscopic determination of the author this point was found to lie at 20.5°C.

The system LiBr–C_2H_5OH. Turner and Bissett[7] observed the existence of the alcoholate $LiBr \cdot 4C_2H_5OH$ and Bonnell and Jones[8] determined the solubility curves of the alcoholate and the anhydrous salt. The congruent m.p. was 23.8°C.

The system LiBr–*n*-C_3H_7OH. The solubilities of the system are not found in the literature, but the existence of the alcoholate $LiBr \cdot 4n\text{-}C_3H_7OH$ was confirmed by Turner and Bissett.[7] The author determined preliminarily the solubilities and obtained the transition point as about 7°C., and the congruent m.p. as 35.8°C.

---

(3) S. E. Simon, *J. prak. Chem.*, **20** (1879), 371.
(4) E. Lloyd, C. B. Brown, D. G. R. Bonnel and W. F. Jones, *J. Chem. Soc.*, **1928**, 658.
(5) The preliminary determination of solubility was carried out on the systems LiCl-CH_3OH and LiBr-*n*-C_3H_7OH, but the results are not given here.
(6) W. E. S. Turner and C. C. Bissett, *J. Chem. Soc.*, **103** (1913), 1904.
(7) W. E. S. Turner and C. C. Bissett, *ibid.*, **105** (1914), 1777.
(8) D. G. R. Bonnel and W. J. Jones, *ibid.*, **1926**, 318.

Apparatus and Method of Procedure.

The apparatus used was similar to that already described.[2] A solution having the composition of the alcoholate was prepared from the pure alcohol and the anhydrous salt in a freezing-point tube with proper precaution against moisture. The tube was placed in the air-jacket immersed in a cooling bath at a temperature about 5°C. below the m.p. When the solution supercooled and the solid alcoholate commenced to separate out without induced by infection, the tube was transferred to the other air-jacket immersed in a thermostat at a temperature of 0.3–0.5°C. below the m.p. and the constant highest temperature was observed by a Beckmann thermometer. In certain cases, however, some crystals of the alcoholate were allowed to remain on melting the solid phase after each measurement and then used as nuclei for crystallisation in the following freezing. After the m.p. of the pure alcoholate was determined, a foreign substance was added into the solution and the same procedure was carried out. Since the molten alcoholate prepared was slightly turbid because of minute amounts of the suspended particles, centrifuging was in some cases applied to it. The clear solution thus obtained showed, however, the same result for the cryoscopic determination.

Preparation of Materials.

Alcohols. With the exception of ethyl alcohol these were dehydrated by aluminium amalgam.[9] The dehydration of ethyl alcohol was carried out by the method of Adickes,[10] using metallic sodium and ethyl formate.

Lithium chloride. Merck's salt was recrystallised from water as hydrate and was dehydrated by heating at 120–130°C.

Lithium bromide. This salt was prepared by the neutralisation of hydrobromic acid with lithium carbonate and then dehydrated at 130°C.

Other substances were purified by ordinary methods.

Experimental Results.

The system LiCl–CH_3OH. The solution of the composition $LiCl{\cdot}3CH_3OH$ was liable to supercooling and the freezing commenced almost always at temperatures below −10°C., much lower than the congruent m.p. 12.9°C. Owing to this fact care was taken not to lose completely the crystalline alcoholate during the cryoscopic experiment.

(9) R. F. Brunel, J. L. Crenshaw and E. Tobin, *J. Am. Chem. Soc.*, **43** (1921), 561.
(10) F. Adickes, *Ber.*, **63** (1930), 2753.

The molecular depressions for 100 g. of the pure alcohol were determined using water and acetone as solutes and the values 38 and 39 were obtained respectively.

The system LiCl–C_2H_5OH. The lowering of the congruent m.p. was measured for the following eight solutes and the constant K was calculated by the relation (1). The results are given in Tables 1 to 7.

Table 1. Solute: Water, mol. wt. = 18.

Weigt of alcohol W in g.	Weight of solute w in g.	Observed lowering of temperature ΔT in °C.	Molecular depression K
31.8	0.159	1.275	45.9
31.7	0.191	1.506	45.0
32.1	0.220	1.733	45.5
32.0	0.273	2.135	45.0
26.4	0.290	2.757	45.3

Mean: 45.3

Table 2. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
31.8	0.346	0.851	45.4
25.7	0.347	1.059	45.5
31.9	0.452	1.102	45.1

Mean: 45.3

Table 3. Solute: Acetanilide, mol. wt. = 135.

W	w	ΔT	K
23.8	0.346	0.491	45.6

Table 4. Solute: Camphor, mol. wt. = 152.

W	w	ΔT	K
31.7	0.348	0.329	45.6
31.7	0.532	0.499	45.2
32.1	0.814	0.752	45.1

Mean: 45.3

Table 5. Solute: Carbon tetrachloride, mol. wt. = 154.

W	w	ΔT	K
31.7	0.765	0.690	44.0
31.3	0.886	0.803	43.7
31.8	0.971	0.864	43.6
33.1	1.459	1.271	44.4

Mean: 43.9

Table 6. Solute: Benzene, mol. wt. = 78.

W	w	ΔT	K
32.1	0.361	0.641	44.5
32.1	0.412	0.717	43.6
32.2	0.457	0.794	43.6
32.1	0.660	1.134	43.0

Mean: 43.7

Table 7. Solute: Toluene, mol. wt. = 92.

W	w	ΔT	K
31.9	0.320	0.481	44.1
32.6	0.470	0.674	43.0
32.5	0.694	0.989	42.6
31.6	0.675	1.004	43.2
31.6	0.715	1.046	42 5

Mean: 43.1

As shown in Tables 5 to 7 non-polar liquids give a little lower values for the constant K. This behaviour may be, as previously described,[2] qualitatively interpreted as follows. The polarity of solute affects the activity of the solvent alcohol and thus on the dissolution of non-polar substances the decrease of this activity is smaller than in the case of polar solutes.

The system LiBr–C_2H_5OH. The molecular depression was determined quite similarly to the foregoing system. The supercooling was less than 1°C. The results are given in Tables 8 to 12.

Table 8. Solute: Water, mol. wt. = 18.

W	w	ΔT	K
31.1	0.046	0.493	60.0
31.6	0.078	0.778	56.8
31.8	0.200	2.023	57.9

Mean: 58.2

Table 9. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
31.4	0.284	0.900	57.7
24.9	0.309	1.217	56.9

Mean: 57.3

Table 10. Solute: Benzoic acid, mol. wt. = 122.

W	w	ΔT	K
31.5	0.117	0.181	59.4

Table 11. Solute: Carbon tetrachloride, mol. wt. = 154.

W	w	ΔT	K
31.5	0.647	0.647	55.3
31.9	1.279	1.428	54.8

Mean: 55.1

Table 12. Solute: Benzene, mol. wt. = 78.

W	w	ΔT	K
31.4	0.245	0.553	55.3
31.5	0.446	0.992	54.7

Mean: 55.0

As shown in Tables 11 and 12 non-polar solutes give a little lower constants as in the foregoing system.

The system LiCl–n-C_3H_7OH. The equilibrium at the congruent m.p. was less stable in comparison with the other systems and the influence of supercooling was greater. Thus the results were somewhat irregular.

Table 13. Solute: Acetone, mol. wt. = 58.

W	w	ΔT	K
33.1	0.251	0.79	60.4
32.8	0.321	1.02	60.5
27.7	0.564	1.96	55.8

Mean: 58.9

Table 14. Solute: Water, mol. wt. = 18.

W	w	ΔT	K
33.1	0.122	1.10	53.7
25.3	0.211	2.48	53.5
32.8	0.293	2.76	55.6

Mean: 54.3

Table 15. Solute: Nitrobenzene, mol. wt. = 123.

W	w	ΔT	K
32.9	0.623	0.91	58.5
32.7	0.654	0.94	57.8

Mean: 58.2

The lower value for water cannot be explained only by these data. This will be discussed after more data are obtained.

Calculation of the Heat of Fusion from the Cryoscopic Constant.

It was shown before[1] that the molecular depression of the transition point at which a crystalline solvate melted to form the anhydrous salt and a saturated solution with regard to this salt could be expressed by the following equation,

$$K = \frac{RT^2}{H} \frac{nM_0}{100} \frac{c}{c+i}, \qquad (2)$$

where R denotes the gas constant, T the absolute transition point, H the heat of fusion per mol of the solvate, n the number of mols of the solvent per mol of the salt in the solvate, M_0 the molecular weight of the pure solvent, c the number of mols of the solvent per mol of the salt in the solution, and i the van't Hoff factor. This factor may be assumed as unity because of the high concentration and the previous result[11] of the vapour pressure determination of the similar system.

In the present case the molten solvate has the same composition as that of the solvate and c is equal to n. Therefore (2) becomes,

(11) H. Oosaka, *Bull. Inst. Phys. Chem. Research* (Tokyo), **10** (1931), 466; Abstracts therefrom, **4** (1931), 48.

$$K = \frac{RT^2}{H}\frac{M_0}{100}\frac{n^2}{n+1}. \qquad (3)$$

Taking the probable value of the constant for polar solutes the heat of fusion was calculated and the results are given in Table 16.

Table 16.

Alcoholate	Congruent m.p. °C.	Molecular depression		Heat of fusion	
		K	$\bar{K}$	kcal. per mol	cal. per g.
$LiCl \cdot 3CH_3OH$	12.9	38	55	3.08	22.2
$LiCl \cdot 4C_2H_5OH$	20.5	45	55	5.60	24.7
$LiBr \cdot 4C_2H_5OH$	23.8	58	85	4.44	16.4
LiBr $4n$-C_3H_7OH	35.8	58	79	6.28	19.2

The values of the cryoscopic constant $\bar{K}$ referred to 100 g. of the solvate are also included in the table for referrence. These were obtained by multiplication of K with $\bar{M}/nM_0$, $\bar{M}$ being the molecular weight of the solvate.

The Abnormal Molecular Depressions when Homologous Alcohols are dissolved as Foreign Substances.

When homologous alcohols were used as solutes in the cryoscopy, abnormally low values of the molecular depression were obtained. The results are given in Tables 17 to 27.

The system $LiCl$-CH_3OH.

Table 17.

Solute	W	w	ΔT	K
C_2H_5OH	24.6	0.601	1.76	33.1
n-C_3H_7OH	23.9	0.490	1.22	35.7
n-C_4H_9OH	23.9	0.336	0.69	36.3
iso-$C_5H_{11}OH$	23.1	0.462	0.82	36.1

The system $LiCl$-C_2H_5OH.

Table 18. Solute: Methyl alcohol, mol. wt. = 32.

W	w	ΔT	K
32.0	0.138	0.473	35.1
31.4	0.421	1.494	35.7
32.1	0.685	2.378	35.7

Mean: 35.5

Table 19. Solute: *n*-Propyl alcohol, mol. wt. = 60.

W	*w*	*ΔT*	*K*
32.1	0.479	0.713	28.7
22.7	0.469	0.953	27.7
31.5	0.660	0.972	27.8
31.9	0.822	1.190	27.7
31.1	0.990	1.534	28.9
24.6	0.914	1.677	27.1
25.0	1.124	2.108	28.1

Mean: 28.0

Table 20. Solute: *n*-Butyl alcohol, mol. wt. = 74.

W	*w*	*ΔT*	*K*
32.7	0.205	0.371	43.8
32.3	0.450	0.835	44.4
33.9	0.494	1.230	44.0
32.3	0.648	1.240	45.7

Mean: 44.5

Table 21. Solute: iso-Amyl alcohol, mol. wt. = 88.

W	*w*	*ΔT*	*K*
31.2	0.197	0.317	44.2
31.6	0.462	0.755	45.4
25.3	0.607	1.268	46.5
31.4	0.803	1.364	46.9
24.0	0.982	2.139	46.0

Mean: 45.8

The system LiBr-C_2H_5OH.

Table 22. Solute: Methyl alcohol, mol. wt. = 32.

W	*w*	*ΔT*	*K*
31.5	0.150	0.620	41.7
31.4	0.278	1.142	41.3

Mean: 41.5

Table 23. Solute: *n*-Propyl alcohol, mol. wt. = 60.

W	*w*	*ΔT*	*K*
23.7	0.433	0.430	14.1
25.0	0.648	0.648	15.0
31.4	1.040	0.789	14.3
31.4	1.172	0.917	14.7
21.9	0.936	0.971	13.6

Mean: 14.3

Table 24. Solute: iso-Propyl alcohol, mol. wt. = 60.

W	*w*	*ΔT*	*K*
32.3	0.416	0.689	32.1
31.8	0.473	0.774	31.2

Mean: 31.7

Table 25. Solute: *n*-Butyl alcohol, mol. wt. = 74.

W	*w*	*ΔT*	*K*
32.3	0.411	0.890	51.8

Table 26. Solute: iso-Amyl alcohol, mol. wt. = 88.

W	*w*	*ΔT*	*K*
25.7	0.361	0.889	55.7
31.5	0.473	0.983	57.6
24.3	0.613	1.659	57.9

Mean: 57.1

The system LiBr-*n*-C_3H_7OH.

Table 27.

Solute	*W*	*w*	*ΔT*	*K*
CH_3OH	26.5	0.481	2.70	47.6
C_2H_5OH	21.9	0.286	0.50	17.6
C_2H_5OH	32.1	0.861	1.06	18.2
n-C_4H_9OH	27.3	0.487	0.93	38.7
iso-$C_5H_{11}OH$	27.5	0.579	1.23	51.4

Consideration on the Anomalous Depression.

The results for the abnormal depression are summarized in Table 28.

Table 28.

Solute	Solvent			
	$LiCl\text{-}CH_3OH$	$LiCl\text{-}C_2H_5OH$	$LiBr\text{-}C_2H_5OH$	$LiBr\text{-}C_3H_7OH$
CH_3OH	Solvent	36	42	48
C_2H_5OH	33	Solvent	Solvent	18
$n\text{-}C_3H_7OH$	36	28	14	Solvent
$iso\text{-}C_3H_7OH$	—	—	32	—
$n\text{-}C_4H_9OH$	36	45	52	39
$iso\text{-}C_5H_{11}OH$	36	46	57	51
The normal value	38	45	58	58

It is clearly seen from the table that the anomaly becomes greater as the molecular weight of the solute alcohol approaches to that of the solvent alcohol. This anomaly may be accounted for by assuming that the solute alcohol forms a solid solution with the solid solvate, and can be formulated by considering vapour pressures of the system. In Fig. 2 the curves AC and BC show the vapour pressures of the pure solid alcoholate and its melt respectively, both dissociating to the anhydrous salt and alcohol vapour. The curve DE represents the vapour pressure of the solid solution and AE that of the liquid solution when a solute forming a solid solution is added to the system. The point C is the congruent m.p. of the pure alcoholate, E the m.p. of the solid solution, hence EF the depression of the m.p. ΔT, AD the depression of vapour pressure for the solid solution Δp_1, and AB that for the liquid solution Δp_2. If one mol of the solid solution contains n_1 mols of the solute alcohol and one mol of the liquid solution n_2 mols, then according to the Raoult's law

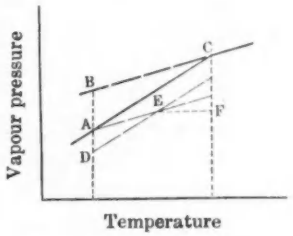


Fig. 2.

$$\Delta p_1 = n_1 p \,, \qquad \text{and} \qquad \Delta p_2 = n_2 p \,,$$

where p is the vapour pressure of the system at the m.p. Considering the geometrical relations of the figure over an infinitesimal range and applying the Clapeyron-Clausius equation the following relation is obtained,

$$n_2-n_1 = \Delta T \frac{q_1-q_2}{RT^2} , \tag{4}$$

where q_1 and q_2 are the molar heats of evaporation of alcohol from the alcoholate and the melt respectively. As the molar heat of fusion H can be represented by the following expression,[1]

$$H = n(q_1-q_2) ,$$

and hence (4) becomes

$$\Delta T = (n_2-n_1)\frac{nRT^2}{H} . \tag{5}$$

When the melt contains w g. of the solute alcohol per W g. of the solvent alcohol,

$$n_2 = \frac{M_0 w}{WM}\left(\frac{n}{1+n}\right) . \tag{6}$$

This relation is approximate but may hold within the experimental error because of the low concentration of the solute alcohol.

If r represents the partition coefficient of the solute alcohol between the liquid and solid solutions, and the solute has the same molecular weight in each phase,

$$r = n_1/n_2 . \tag{7}$$

The constancy of the values of r can be seen from that of the values of K indifferent to the concentration. By using (6) and (7), (5) becomes

$$\Delta T = (1-r)\left(\frac{RT^2}{H}\frac{M}{100}\frac{n^2}{1+n}\right)\frac{100w}{WM} ,$$

where the term in the second brackets is the normal constant K already referred to. If the cryoscopic constant in the abnormal case is K', then

$$K' = (1-r)K .$$

In order to test this relation experimentally, tetra-alcoholate of lithium chloride as solvent and n-propyl alcohol as solute were chosen

and the constant r was determined by measuring the concentrations of the solute alcohol in the liquid and solid phases in equilibrium, using a Zeiss water-interferometer. This experiment accompanied some difficulties on account of the similarity of the alcohols, the small concentration of the solute alcohol and the existence of salt in the solution, and besides the separation of both phases was not complete. The results were accordingly not very accurate but the value of r thus observed was in approximate accordance with the value calculated from the values K and K' which were in turn determined by the cryoscopic experiment.

Summary.

(1) The lowerings of the congruent melting points of the alcoholates: $LiCl \cdot 3CH_3OH$, $LiCl \cdot 4C_2H_5OH$, $LiBr \cdot 4C_2H_5OH$, and $LiBr \cdot 4n\text{-}C_3H_7OH$ by the addition of foreign substances have been measured and the molecular depressions referred to 100 g. of each alcohol have been determined.

(2) From these cryoscopic constants the heats of fusion of the alcoholates have been calculated.

(3) When homologues of the solvent alcohol have been used as solutes, abnormally low values have been obtained for the cryoscopic constant. This discrepancy may be considered as due to the formation of a solid solution between the alcoholate and the solute alcohol and this fact has been semi-quantitatively verified.

In conclusion the author expresses his hearty thanks to Professor M. Katayama for his continued interest and advice throughout this series of research. Thanks are also due to Professor I. Wada for giving to the author facilities for carrying out this work.

Chemical Laboratory, Tokyo Bunrika University,
Koishikawa, Tokyo.

On the Relation between the Configuration of Metallic Complex Salts and their Absorption Spectra.[1]

By Hideo SUEDA.

(Received April 24th, 1937.)

Introduction. Many valuable but qualitative conclusions on the absorption spectra of metallic complex salts have already been obtained by Y. Shibata[2]. By means of quantitative studies, R. Luther and A. Nikolopulos[3], R. I. Colmar and F. W. Schwartz[4] and A. Mead[5] have also found that whenever a certain substitution occurs in a complex radical, a constant change of the maximum absorption is consequently produced. But, as these authors did not take notice of the position of those substituents, their point of view cannot generally apply to all complex salts. I. Lifschitz[6], expressing his interest in his work about the relation between the absorption and the stereoisomer, could not obtain any conclusion on it. A. Uspenski and A. Bamdas[7] have recently measured the absorption of some isomers, and have only reported that the position of maximum absorption of cis-salts corresponds to that of the minimum absorption of trans-salts. In fact, no papers have as yet appeared in which the absorptions of complexes were quantitatively discussed with a stereochemical consideration.

Thereupon, it seemed very interesting to the author to study this question. In the present research, I have found a new relation between the configuration of nitro-ammine-cobaltic salts and their absorption spectra, and have applied it to the other series of complex salts.

Nitro-ammine-cobaltic complex salts. As these salts are comparatively stable and prepared in a pure state forming a most perfect series of compounds, they are the best materials for the author's purpose of study. Although their absorption spectra have been individually

(1) Summarized the author's two reports already published in Japanese: *J. Chem. Soc. Japan*, **57** (1936), 406, 542.
(2) Y. Shibata, *J. Coll. Sci., Tokyo Imp. Univ.*, **37** (1915), Art. 2.
(3) *Z. physik. Chem.*, **82** (1913), 361.
(4) *J. Am. Chem. Soc.*, **54** (1932), 3204.
(5) *Trans. Faraday Soc.*, **30** (1934), 1053.
(6) "Spektroskopie u. Kolorimetrie", 2. Aufl., 228 (1927).
(7) *Trans. Inst. Pure Chem. Reagents* (U.S.S.R.), No. 13 (1933), 48; *Chem. Abstracts*, **27** (1933), 4736.

measured by many authors[8], only Y. Shibata has studied all nitro-compounds of the series. H. Ley and Y. Shibata have discovered that *trans*-dinitro-tetrammine-cobaltic salts have an absorption band at 4000 mm.$^{-1}$ of the wave number, i.e. the third band, that is wanted in the cis-isomers. Y. Shibata has also indicated that two of the nitro-radicals in trinitro-triammine- and tetranitro-diammine-cobaltic salts must occupy the trans-position on account of the existence of this third band. Still, I have studied on the absorption band in the neighbourhood of 320–350 mμ of wave length, i.e. the second band, and have found that this band changes owing to the position and the number of nitro-radicals in the complex salts.

Comparison of the absorption curves[9]. (1) $[Co(NH_3)_5(NO_2)]Cl_2$ and *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$. The absorption curves of both salts (curves A and B in Fig. 1) are similar except in their extinction coefficients: both have their maximum absorption at 325 mμ of wave length. The comparison of their extinction coefficient shows that the absorption power of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ is about double that of $[Co(NH_3)_5(NO_2)]Cl_2$. This absorption curve of pentammine-salt is different from that given in the paper of R. Samuel[8], but similar to that of $[Co(NH_3)_5(NO_2)]SO_4$ obtained by R. Samuel and M. Uddin[10].

(2) *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ and *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$. The maximum absorption of these salts is different from each other, i.e. that of cis-salt is found at 325 mμ showing $\log \varepsilon = 3.46$ (ε denotes an extinction coefficient) at this wave length, but the trans-salt (curve C in Fig. 1) gives its maximum absorption at 347 mμ and $\log \varepsilon = 3.55$ at that wave length. The trans-salt is more hyperchromic and more bathochromic than the cis-salt, and this is analogous to the Ley's curves measured qualitatively. In spite of the difference of position and intensity of the absorption bands, both absorptions are found to be almost coincident at 270–280 mμ of wave length[11].

(3) $[Co(NH_3)_3(NO_2)_3]$. This salt has the maximum absorption near 340 mμ of wave length where $\log \varepsilon$ is 3.65 (curve D in Fig. 1). For

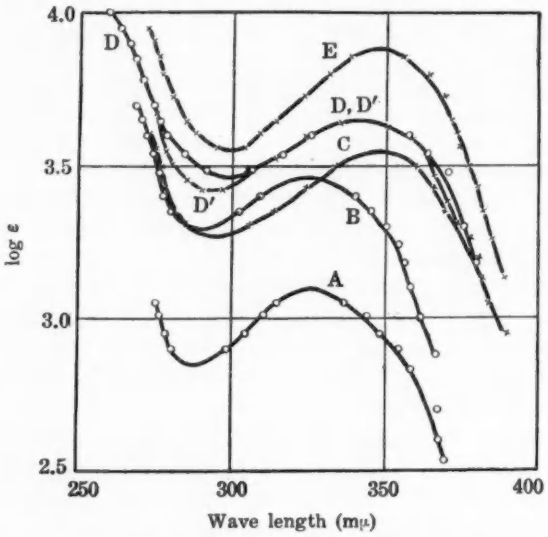
(8) A. Hantzsch, *Z. physik. Chem.*, **70** (1910), 372; H. Ley and H. Winkler, *Ber.*, **45** (1912), 372; A. Piutti, *Ber.*, **45** (1912), 1830; R. Luther and A. Nikolopulos, *Z. physik. Chem.*, **82** (1913), 361; Y. Shibata, *J. Chem. Soc. Japan*, **30** (1915), 1243; R. Samuel, *Z. Physik*, **70** (1931), 43.

(9) Measured by the author, this Bulletin, **12** (1937), 71.

(10) *Trans. Faraday Soc.*, **31** (1935), 423.

(11) The author thinks that the electric valencies of complex ions have a certain relation with their absorption which exists in their shorter wave length as in this case. Refer also to the paper: T. Uemura and H. Sueda, this Bulletin, **10** (1935), 267.

a reason which will be explained later, I have arbitrarily selected fifteen wave lengths between 275 mμ and 380 mμ by using the absorption coefficients of *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ and that of $[Co(NH_3)_5(NO_2)]Cl_2$, and the extinction coefficients corresponding to these selected wave lengths were added to form a curve D′ in Fig. 1. Curve D′ is therefore traced



A $[Co(NH_3)_5(NO_2)]Cl_2$ D $[Co(NH_3)_3(NO_2)_3]$
B *cis* $[Co(NH_3)_4(NO_2)_2]Cl$ D′ A+C
C *trans* $[Co(NH_3)_4(NO_2)_2]Cl$ E $K[Co(NH_3)_2(NO_2)_4]$

Fig. 1.

by mixing one mol of each salt, and it should be assumed as a curve expressing one mol. Curves D and D′ in Fig. 1 show a good coincidence in the position and the intensity of the absorption band, but a slight difference can be seen only in the shorter wave length below 300 mμ.

(4) *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ and $K[Co(NH_3)_2(NO_2)_4]$. The curves given by these two salts are similar except their absorption power: both have the maximum absorption at 347 mμ. The relation of the absorption powers shown by both salts is perfectly the same as in case (2), i.e. the absorption power of $K[Co(NH_3)_2(NO_2)_4]$ is double that of *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$.

Discussion. It is generally accepted that an absorption of the co-ordinatedly saturated complex ion is due to a mutual action produced between a central ion and co-ordinated atomic groups. In the above comparison, cobalt is selected as the central atom and only ammonia molecules and nitro-radicals are co-ordinated in the complex ion, so the difference which occurs in the absorption can be considered in connection with the configuration of complex ions, whatever the mechanism of the light absorption may be. It is convenient to say that the absorption capacity due to the ammonia molecules which are co-ordinated with cobalt atom is very weak in comparison with that of nitro-radicals, i.e. the extinction coefficient of the maximum absorption given by $[Co(NH_3)_6]Cl_3$ is only about 40 (at 336 mμ)[12], while that given by $[Co(NH_3)_5(NO_2)]Cl_2$, the weakest absorbent of nitro-ammines, expresses 1260 (at 325 mμ). As an additivity can apply to the intensity of light absorption, an absorption given by nitro-ammine-cobaltic salts may be supposed only with the nitro-radicals, in neglecting the influences due to ammonia molecules.

According to Werner's co-ordination theory, we can safely conclude that any groups co-ordinated with the hexacovalent central ion can have no positions but cis and trans.

In comparison (1), the complex ion containing two nitro-radicals in cis-position shows that its absorption band is situated almost similarly to that given by the complex which has only one nitro-radical, but the absorption capacity of the former is nearly double that of the latter. In this case, no change on the position of the absorption band and the increase in extinction coefficients can tell me that the mutual actions between the cis-co-ordinated groups are themselves so weak that they are negligible. It is also true that the action upon the central atom of two co-ordinated groups which occupy cis-position is nearly identical when the groups is alone in a complex radical, and they show only the additivity. An analogous case can be found in organic dyes which contain several identical chromophores in the molecule, and these chromophores cannot be supposed to react one upon another from the constitution. J. D. Piper and W. R. Brode[13] have recently reported that, in such a case, the absorption band does not change its position, and its absorption capacity is increased in proportion to the number of chromophores.

From comparison (2), when two nitro-radicals take the trans-position in a complex radical, the position of the absorption band due to these

(12) T. Uemura and H. Sueda, this Bulletin, **10** (1935), 50; R. Samuel, *loc. cit.*; J. Kranig, *Arch. phys. biol.*, **7** (1929), 148.

(13) *J. Am. Chem. Soc.*, **57** (1935), 135.

radicals is different from that given by a cis-compound, and the absorption capacity is also slightly different in these cases. It can be proved that these spectrochemical differences based on stereoisomers are produced by the central ion and co-ordinated groups and also by the stereochemical configuration that must be taken into account. When these co-ordinated groups are supposed to take a position at every corner of a regular octahedron having some influences upon the central ion, the influence of a co-ordinated group upon the centre may be said to have the deepest relation to that which is situated on its opposite side. The consequence of this consideration is that the most important factor to control the position of an absorption band must be a pair of co-ordinated groups situated in trans-position. The existence of a characteristic absorption band due to such a pair of groups which occupy the trans-position may be assumed, and the author has provisionally given the name of "characteristic absorption" to such an absorption. On the other hand, as the influence against an absorption given by cis-group is not found on the position of bands but only an additivity can be observed, we can make the following assumption: an absorption due to a metallic complex ion is represented by the sum of characteristic absorption given by the pair of groups occupied in trans-position in a co-ordinated complex. It is very important to analyse an absorption spectrum of a solution to give it a theoretical meaning, and Y. Shibata and K. Harai[14] as well as others[15] have already studied this question. Although the idea proposed by the present author is somewhat hypothetical, yet, it may also be recognized as a kind of analysis for an absorption spectrum of complex salt solutions.

With this assumption, the absorption spectra of nitro-ammine salts can be explained as follows: the absorption of *cis*-$[Co(NH_3)_4(NO_2)_2]Cl$ is assumed as a sum of three characteristic absorptions, i.e. $(NH_3\text{-}Co\text{-}NH_3)$[16] and $2(NH_3\text{-}Co\text{-}NO_2)$ (see Fig. 2). The absorption of $[Co(NH_3)_5(NO_2)]Cl_2$ can also be resolved into $2(NH_3\text{-}Co\text{-}NH_3)$ and $(NH_3\text{-}Co\text{-}NO_2)$. Since $(NH_3\text{-}Co\text{-}NH_3)$ can be neglected in comparison with $(NH_3\text{-}Co\text{-}NO_2)$, as described before, the absorption given by both salts shows therefore that, due to the number of $(NH_3\text{-}Co\text{-}NO_2)$ contained,

(14) *J. Chem. Soc. Japan*, **56** (1935), 1.

(15) W. R. Brode, *Proc. Roy. Soc.* (London), A, **118** (1928), 286; *J. Am. Chem. Soc.*, **56** (1934), 1842.

J. P. Mathiue (*Bull. soc. chim.*, [5], **3** (1936), 463) has recently reported a very interesting relation between the constitution of co-ordinated complex salts and the separation of their absorption bands.

(16) This symbol represents the characteristic absorption assumed to be produced by two ammonia molecules in trans-position having cobalt as the central ion.

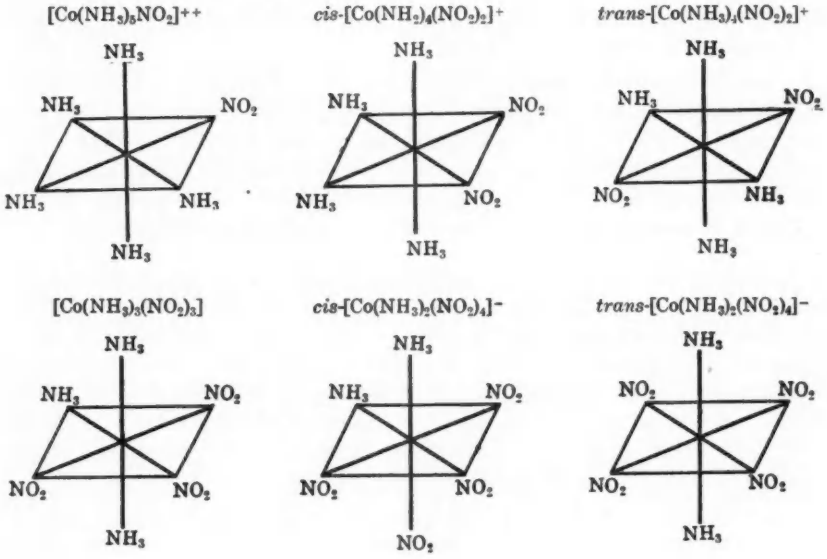


Fig. 2.

the former cis-compound has double the absorption intensity of the latter pentammine-complex showing similar curves. With regard to the *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$, its absorption may be considered as the sum produced by $2(NH_3\text{-}Co\text{-}NH_3)$ and $(NO_2\text{-}Co\text{-}NO_2)$, and it is almost the same with $(NO_2\text{-}Co\text{-}NO_2)$.

This point of view is also held in comparison (3). Y. Shibata has already determined the configuration of $[Co(NH_3)_3(NO_2)_3]$ as described in Fig. 2, i.e. two of nitro-radicals are in trans-position. Its absorption can therefore be resolved into $(NH_3\text{-}Co\text{-}NH_3)$, $(NH_3\text{-}Co\text{-}NO_2)$ and $(NO_2\text{-}Co\text{-}NO_2)$. So, it is expected that the absorption might be represented as a sum of those given by $[Co(NH_3)_5(NO_2)]Cl_2$ and *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$ by neglecting the effect of $(NH_3\text{-}Co\text{-}NH_3)$ as before. Curve D′ in Fig. 1, traced by taking this sum, shows a good coincidence especially in the band with the observed curve D obtained from the complex $[Co(NH_3)_3(NO_2)_3]$.

The configuration of $K[Co(NH_3)_2(NO_2)_4]$ has not yet been determined. Y. Shibata, T. Maruki[17] and W. Thomas[18] have already

(17) *J. Coll. Sci., Tokyo Imp. Univ.*, **41** (1917), Art. 2.
(18) *J. Chem. Soc.*, **123** (1923), 617.

given a cis-configuration to the compound, while E. H. Riesenfeld and R. Klement[19], a trans-configuration.

As shown in the comparison (4), the absorption intensity due to the complex $K[Co(NH_3)_2(NO_2)_4]$ is nearly twice that of the *trans*-$[Co(NH_3)_4(NO_2)_2]Cl$. According to the above-mentioned idea, this is easily understood by assuming that $K[Co(NH_3)_2(NO_2)_4]$ may contain two (NO_2-Co-NO_2) in its complex radical. The author wishes to give a trans-configuration (see Fig. 2) to this Erdemann's salt.

Application of the above-mentioned assumption to aquo-chloro-ammine salts of cobalt and chromium. In the case of the already described nitro-ammine complex salts, as their absorption capacity is so remarkably increased by the nitro-radical that the influence due to (NH_3-Co-NH_3) can be neglected, the discussion becomes comparatively simple. But to give more weight to the assumption, the author has tried to apply it to the cases where the absorptions are little influenced by the substitution which occurs in a complex radical.

According to the author's assumption, when two or three absorption curves are known for some compounds in a series, a characteristic absorption can be deduced, and an absorption of an other salt can be assumed by a suitable combination of those characteristic absorptions. To verify this assumption, observed curves were compared with those which are assumed from the characteristic curves.

(1) *Absorption curves given by cobalti-ammine complex salts in visible region.* Absorption curves of $[Co(NH_3)_6]Cl_3$[20], $[Co(NH_3)_5(H_2O)]Cl_3$[20], $[Co(NH_3)_4(H_2O)_2]Cl_3$[20], $[Co(NH_3)_5Cl]Cl_2$[20], $[Co(NH_3)_4Cl(H_2O)]Cl_2$[21] and *cis*-$[Co(NH_3)_4Cl_2]Cl$[21] were used for calculation.

According to my assumption, the absorption of $[Co(NH_3)_6]Cl_3$ should be three times the characteristic absorption (NH_3-Co-NH_3). The absorption of $[Co(NH_3)_4(H_2O)_2]Cl_3$ should be represented by the sum of (NH_3-Co-NH_3) and 2(NH_3-Co-H_2O), as this complex salt is supposed to take cis-configuration. Therefore, (NH_3-Co-H_2O) can be calculated by deducting (NH_3-Co-NH_3), which is given as 1/3 of the absorption $[Co(NH_3)_6]Cl_3$, from the absorption of $[Co(NH_3)_4(H_2O)_2]Cl_3$ and

(19) *Z. anorg. allgem. Chem.*, **124** (1922), 1.

(20) The absorption data of these salts were transferred from Colmar and Schwartz's work (*loc. cit.*).

(21) The absorption data of these salts were obtained from the curves published in the paper by Luther and Nikolopulos (*loc. cit.*).

dividing the difference in two. By combining (NH_3-Co-NH_3) and (NH_3-Co-H_2O), the value of "2(NH_3-Co-NH_3)+(NH_3-Co-H_2O)" can easily be deduced as the calculated value corresponding to the absorption shown by $[Co(NH_3)_5(H_2O)]Cl_3$. This calculation gives a good coincidence with the observation as seen in Table 1.

Table 1[22].

λ (mμ)	$[Co(NH_3)_6]Cl_3$	(NH_3-Co-NH_3)	$\left[\begin{matrix}Co(NH_3)_4\\(H_2O)_2\end{matrix}\right]Cl_3$	(NH_3-Co-H_2O)	$[Co(NH_3)_5(H_2O)]Cl_3$	
					obs.	calc.
450	46.1	15.4	22.4	3.5	34.9	34.3
460	53.8	17.9	30.4	6.3	40.8	42.1
470	56.1	18.7	36.4	8.9	45.5	46.3
480	55.5	18.5	44.9	13.2	46.5	50.2
490	49.1	16.4	49.5	16.6	47.9	49.4
500	33.6	11.2	52.9	20.9	45.5	43.3
520	18.9	6.3	49.1	21.4	39.2	34.0
540	5.7	1.9	39.3	18.7	25.9	22.5
560	0.4	0.1	26.2	13.4	13.6	13.6

The value of (NH_3-Co-Cl) can be obtained from (NH_3-Co-NH_3) and the absorption data shown by $[Co(NH_3)_5Cl]Cl_2$ which should be represented as "2(NH_3-Co-NH_3)+(NH_3-Co-Cl)". As $[Co(NH_3)_4(H_2O)Cl]Cl_2$ takes a cis-configuration, its absorption should be given by "(NH_3-Co-NH_3)+(NH_3-Co-H_2O)+(NH_3-Co-Cl)". As Table 2 indicates, the sum of these characteristic absorptions obtained from calculation are somewhat greater than the observed values, but the position of the maximum absorption band is nearly matched.

The absorption of *cis*-$[Co(NH_3)_4Cl_2]Cl$ can be resolved into "(NH_3-Co-NH_3)+2(NH_3-Co-Cl)", and the calculated values are also much greater than the observed data, although a coincidence for the position of the absorption band can be recognized. A part of the discordance of calculated and observed values in extinction coefficients comes perhaps

(22) The numerical data in the tables used in this paper are shown in extinction coefficient (ε), defined from the formula: $\log I_0/I = \varepsilon cd$, where I_0 and I represent respectively the light intensity given before and after its transmission; c, concentration of solution in mol; d, layer length of solution in cm.

from the difficulty of accurate measurement which is due to the instability of the salt in aqueous solution.

Table 2.

λ (mμ)	$\left[\begin{matrix}Co(NH_3)_5\\Cl\\Cl_2\end{matrix}\right]$	(NH_3-Co-Cl)	$[Co(NH_3)_4(H_2O)Cl]Cl_2$		*cis*-$[Co(NH_3)_4Cl_2]Cl$	
			obs.	calc.	obs.	calc.
450	24.2	-6.6	16	12.3	15.5	2.2
460	30.4	-5.4	20	18.8	20	7.1
470	33.4	-4.0	25	23.6	25	10.7
480	37.5	0.5	29.5	32.2	29.5	19.5
490	40.9	8.1	35	41.1	35	32.6
500	43.1	20.7	40	52.8	41	52.6
520	47.5	34.9	46.5	62.6	48	76.1
540	44.0	40.2	48	60.8	48	82.3
560	34.6	34.4	33	47.8	41	68.9

(2) *Absorption curves given by chromi-ammine complex salts in visible and ultraviolet regions.* $[Cr(NH_3)_6]Cl_3$[23], $[Cr(NH_3)_5(H_2O)]Cl_3$[23], $[Cr(NH_3)_4(H_2O)_2]Cl_3$[23], $[Cr(NH_3)_3(H_2O)_3]Cl_3$[23], $[Cr(NH_3)_2(H_2O)_4]Cl_3$[20] and $[Cr(H_2O)_6]Cl_3$[20] were taken for calculation. Analysis and synthesis of the absorption curves can be performed in the same manner when applied to the cobalt-ammines. The value of (NH_3-Cr-H_2O) was obtained from the absorption of $[Cr(NH_3)_3(H_2O)_3]Cl_3$, and that of (NH_3-Cr-NH_3), from the absorption given by $[Cr(NH_3)_5(H_2O)]Cl_3$ and (NH_3-Cr-H_2O). By combining these characteristic absorptions, the calculated values of $[Cr(NH_3)_4(H_2O)_2]Cl_3$ and $[Cr(NH_3)_6]Cl_3$ were deduced. These are compared with the observed data in Table 3. Next, the absorption of $[Cr(NH_3)_2(H_2O)_4]Cl_3$ was calculated from the value of (H_2O-Cr-H_2O) which is given from $[Cr(H_2O)_6]Cl_3$, and that of (NH_3-Cr-H_2O) for comparing with the observed data. These observed and calculated values are considered as showing a passable coincidence in Table 3.

(23) The absorption data in the visible region of these salts were taken from Colmar and Schwartz's publication (*loc. cit.*), and those in ultraviolet from the curves measured by Uemura and Sueda (*loc. cit.*).

Table 3.

λ(mμ)	$[Cr(NH_3)_3(H_2O)_3]Cl_3$	$(NH_3\text{-}Cr\text{-}H_2O)$	$[Cr(NH_3)_5(H_2O)]Cl_3$	$(NH_3\text{-}Cr\text{-}NH_3)$	$[Cr(NH_3)_4(H_2O)_2]Cl_3$		$[Cr(NH_3)_6]Cl_3$	
					obs.	calc.	obs.	calc.
320	6	2	8	3	7	7	8	9
330	9	3	15	6	10	12	18	18
340	11	4	19	8	14	16	22	24
350	15	5	24	9	18	19	28	27
360	19	6	29	12	23	24	29	36
370	23	8	30	11	26	27	21	33
380	26	9	26	9	28	27	16	27
390	29	10	23	7	25	27	10	21
400	29	10	20	5	22	25	7	15
410	26	9	20	6	19	24	7	16
420	23	8	21	7	—	—	14	21
450	12.2	4.1	26.7	11.3	19.7	19.5	36.1	33.9
460	16.5	5.5	31.9	13.2	22.8	24.2	40.8	39.6
470	18.7	6.2	34.1	14.0	26.6	26.4	39.2	42.0
480	22.0	7.3	35.4	14.0	30.5	28.6	33.8	42.0
490	25.6	8.5	34.4	13.0	30.9	30.0	27.5	39.0
500	26.1	8.7	31.5	11.4	30.6	28.8	19.7	34.2
510	25.4	8.5	27.8	9.7	28.1	26.7	12.6	29.1
520	24.8	8.3	21.9	6.8	24.0	23.4	8.4	20.4
530	22.0	7.3	17 2	5.0	19.8	19.6		
540	19.7	6.6	12.1	2.8	14.4	16.0		
550	16.7	5.6	9.4	1.9	10.0	13.1		

λ (mμ)	$[Cr(H_2O)_6]Cl_3$	$(H_2O\text{-}Cr\text{-}H_2O)$	$[Cr(NH_3)_2(H_2O)_4]Cl_3$	
			obs.	calc.
500	3.6	1.2	19.1	18.6
510	4.3	1.4	20.1	18.4
520	5.0	1.7	20.6	18.3
530	5.8	1.9	20.2	16.5
540	6.7	2.2	19.3	15.4
550	7.4	2.5	16.7	13.7

Consideration on results. Some discordances between the calculated and observed values were found in the above comparison. I think that the causes of this difference come first from the weakness of the assumption itself and secondly from the experimental error produced by the quantitative measurement of absorption.

The weakness of the assumption is due to the complete neglect of the influence given by the groups situated in cis-position. If the oscillations of the co-ordinated groups for central ion may be supposed to have an effect upon an absorption, some influences, produced by the groups in cis-position, would be naturally taken into account, though they might be slight. So, it is sure that one of the causes has appeared in adopting the data which are neglected for the corrections due to the cis-groups.

The second cause can of course be considered as nearly inevitable. For the purpose of ascertaining the number of experimental errors produced by an absorption measurement, I have taken an example of results given by R. I. Colmar, F. W. Schwartz[4] and F. W. Beyer[24] for the absorption of $[Co(NH_3)_6]Cl_3$. The mean difference in the extinction coefficients measured by these authors was found to be about 8% between 450 mμ and 500 mμ of wave length.

Strictly speaking, the assumption that I have proposed, needs some corrections. But the author believes his assumption can afford a means to determine the configurations of complex salts within a limit of the present accuracy of absorption measurement. It may also suggest some physical meanings on light absorption of complex salts.

Summary.

(1) From the comparison of absorption curves given by nitro-ammine-cobaltic complex salts near 360 mμ of wave length, the following assumption was deduced: the absorption band presented by complex salt solutions can be resolved into the elements (characteristic absorption) which are due to the pairs of co-ordinated groups situated in transposition in a complex radical, and these elements show an additive property in the same complex ion.

(2) By taking into account of the above-mentioned point of view, $K[Co(NH_3)_2(NO_2)_4]$ (Erdemann's salt) should have a trans-configuration.

(3) This assumption may also be applied to the absorptions given by aquo-chloro-ammine salts of cobalt and chromium, in visible and ultra-violet regions.

In conclusion, the author wishes to express his sincere thanks to Prof. Y. Shibata of the Imperial University of Tokyo, and also to Assist. Prof. T. Uemura of the Tokyo University of Engineering for their kind encouragements.

Laboratory of Inorganic Chemistry,
Tokyo University of Engineering (Tokyo Kôgyô-Daigaku).

(24) *Z. Physik*, **83** (1933), 806.

Studies on the Flow of Gaseous Mixtures through Capillaries. I. The Viscosity of Binary Gaseous Mixtures.

By Hiroshi ADZUMI.

(Received April 24th, 1937.)

Introduction.

When a gas flows through capillaries, the flowing formula is not unique over a wide range of pressure but depends on the proportions of the mean free path and the diameters of the capillaries, and three following cases can be distinguished: (1) If the mean free path is very small in comparison with the diameter the flowing quantity is inversely proportional to the viscosity coefficient of the gas. Such flow is called Poiseuille's or the viscous flow, and the rate of flow can be used as a means of determining the viscosity. (2) If the mean free path is large in comparison with the diameter the flowing quantity is independent of the viscosity but inversely proportional to the square root of the molecular weight of the gas, and such flow is called Knudsen's or the molecular flow. (3) When the mean free path is comparable with the diameter the mode of flow is a mixture of the above two types.

The object of the author's study is to know how gaseous mixtures flow through capillaries under various conditions and in this paper the case where the pure viscous flow takes place is treated.

Viscosities of gaseous mixtures have been measured by many authors. Viscosity—composition curves are in general not straight and some mixtures show maximum values. Several formulæ to express the viscosity of gaseous mixtures, have been given by Maxwell[1], Puluj[2], Sutherland[3], Thiessen[4], Enskog[5], and others, but these formulæ do not represent satisfactorily the results of observations. The conditions for the occurrence of a maximum point were also discussed by many authors in special cases but not considered generally.

The present author measured the viscosities of some gaseous mixtures of organic compounds, and considered the conditions for the occurrence of a maximum point for a general case. The results will be reported below.

(1) Maxwell, *Phil. Mag.*, (IV), **35** (1868), 212.
(2) Puluj, *Sitzber. Akad. Wiss. Wien, Math.-naturw. Klasse*, Abt. IIa, **79** (1879), 97, 745.
(3) W. Sutherland, *Phil. Mag.*, (V), **40** (1895), 421.
(4) M. Thiessen, *Verh. deut. phys. Ges.*, **4** (1902), 348.
(5) Enskog, *Inaug. Diss. Upsala*, (1917).

Experimental.

Viscosimeter. The method of measuring the viscosity is a transpiration type devised by T. Titani[6] and the capillary of the viscosimeter has the following dimensions: internal diameter, about 0.19 mm.; length, about 79 cm.

By measuring the time of flow of a definite volume of the gas (ca. 0.85 c.c. of about 1 atm. pressure) and taking air as a standard substance the viscosity for other gases can be determined relatively. As the separation of gaseous mixtures into components caused by flowing through capillaries is negligible under the experimental conditions, mixtures are treated by the same method as in the case of a simple gas. The temperatures of measurements are between 20° and 100°C.

Apparatus for Mixing Gases. The apparatus is shown schematically in Fig. 1. Cylindrical vessels A and B, each having a capacity of about 200 c.c., are connected with a capillary tube, about 2 mm. in diameter,

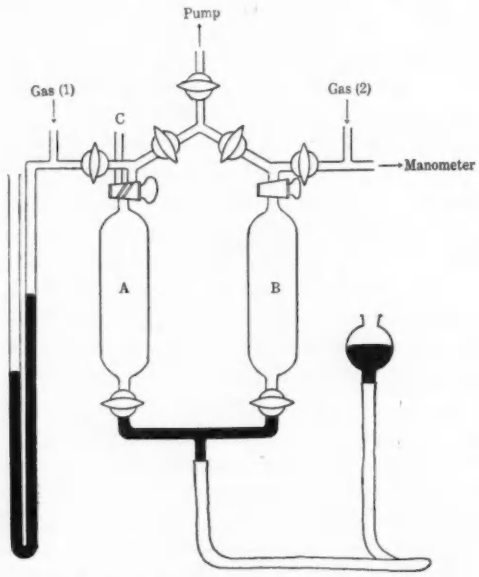


Fig. 1. Apparatus for Mixing Gases.

(6) T. Titani, this Bulletin, **4** (1929), 277.

provided with stopcocks. After evacuation, A and B are filled with the required quantity (read with pressure) of gases to be mixed and then by means of a mercury reservoir the gas in B is driven into A. By the equation of state of gas the molar composition of the mixture is calculated. After standing overnight, the homogeneous mixture is taken out from D.

Preparation of Gases. The preparation of gases used for experiments is as follows: *Hydrogen*: Obtained by the electrolysis of water from 30% sodium hydroxide solution, washed with conc. sulphuric acid, neutral potassium permanganate solution, basic sodium hydrosulphite sloution and then dried with calcium chloride and phosphorous pentoxide, the trace of oxygen being thoroughly removed by passing the gas over red-heated copper wire netting beforehand.

Methane and ethane: Prepared with great care by Dr. J. Horiuti. Methane was obtained from aluminium carbide and water, and ethane by the electrolysis of potassium acetate.

Acetylene: Prepared from calcium carbide and water, passed through sodium hydroxide, washed with solutions of ferric nitrate, copper sulphate, mercuric nitrate, and nitric acid, and finally acidic mercury chloride solution, then dried with calcium chloride. The sample thus purified was condensed with liquid air and carefully fractionated several times.

Propane: Obtained by the action of dilute alcoholic solution of iso-propyl alcohol on Zn-Cu couple[7], washed with fuming sulphuric acid, 2% of potassium permanganate solution, potassium hydroxide solution (1:1), then condensed and fractionated.

Propylene: Obtained by dehydration of iso-propyl alcohol with hot-concentrated phosphoric acid, washed with dilute sodium hydroxide solution and water, then condensed and fractionated.

Results of Measurements. (I) *Simple gases.* Viscosities of six following gases are shown in Table 1: H_2, CH_4, C_2H_2, C_2H_6, C_3H_6, C_3H_8. Sutherland's formula has been found to be applicable for all gases with satisfactory results. The viscosity values calculated by this formula are given in the table.

(7) Glastone and Tribe, *J. Chem. Soc.*, **45** (1884), 154.

Table 1. Viscosities of Simple Gases.

t°C.	Hydrogen $\eta = 68.4\frac{T^{\frac{3}{2}}}{T+79}\cdot10^{-7}$		Methane $\eta = 103.9\frac{T^{\frac{3}{2}}}{T+170}\cdot10^{-7}$		Acetylene $\eta = 104.5\frac{T^{\frac{3}{2}}}{T+220}\cdot10^{-7}$	
	$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	877	—	1059	—	957
20	924	923	1125	1126	1022	1022
30	942	945	1171	1159	1055	1054
40	965	967	1191	1192	1085	1086
50	989	988	1220	1224	1114	1117
60	1008	1009	1255	1256	1146	1149
70	1032	1030	1289	1287	1180	1179
80	1048	1050	1316	1318	1208	1210
90	1072	1070	1345	1348	1246	1240
100	1090	1090	1380	1379	1274	1270

t°C.	Ethane $\eta = 106.0\frac{T^{\frac{3}{2}}}{T+280}\cdot10^{-7}$		Propane $\eta = 99.8\frac{T^{\frac{3}{2}}}{T+318}\cdot10^{-7}$		Propylene $\eta = 100.5\frac{T^{\frac{3}{2}}}{T+302}\cdot10^{-7}$	
	$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
0	—	865	—	762	—	789
20	928	928	—	820	—	848
30	960	959	845	848	876	876
40	991	990	873	876	904	905
50	1016	1021	908	904	935	934
60	1051	1051	932	932	960	962
70	1080	1081	961	959	995	990
80	1109	1111	988	987	1016	1018
90	1143	1140	1013	1014	1048	1045
100	1171	1170	1040	1041	1070	1073

(II) *Gaseous mixtures.* Viscosities of seven following mixtures are given in Tables 2–8: $H_2\sim CH_4$, $H_2\sim C_2H_2$, $H_2\sim C_2H_6$, $H_2\sim C_3H_6$, $CH_4\sim C_2H_2$, $C_2H_2\sim C_3H_6$, $C_3H_6\sim C_3H_8$. The formula used for calculation of viscosities will be discussed later.

Table 2. Viscosities of $H_2 \sim CH_4$. (Fig. 2.)

General formula: $\eta = \dfrac{\eta_{H_2}}{1+\dfrac{n_2}{n_1}1.309\dfrac{T+169}{T+79}} + \dfrac{\eta_{CH_4}}{1+\dfrac{n_1}{n_2}0.478\dfrac{T+169}{T+170}}$

H_2 %	CH_4 %	100°		60°		20°	
		$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1008	1008	924	924
79.17	20.83	1271	1263	1160	1159	1052	1048
69.91	30.09	1312	1305	1190	1194	1074	1078
50.96	49.04	1359	1360	1234	1237	1110	1112
31.05	68.95	1380	1379	1254	1256	1126	1128
0.00	100.00	1380	1380	1255	1255	1125	1125

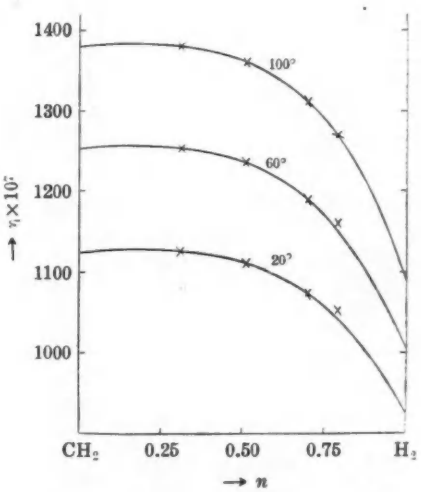


Fig. 2. $H_2 \sim CH_4$

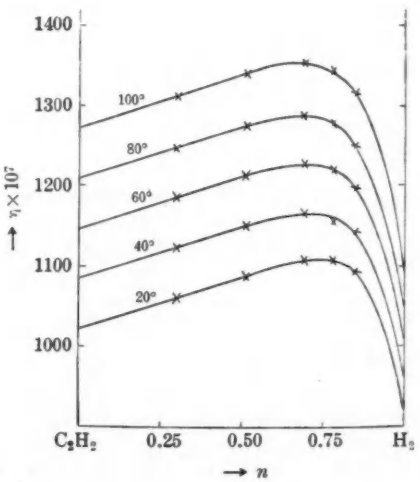


Fig. 3. $H_2 \sim C_2H_2$

Table 3. Viscosities of $H_2 \sim C_2H_2$. (Fig. 3.)

General formula: $$\eta = \frac{\eta_{H_2}}{1+\frac{n_2}{n_2}1.478\frac{T+157}{T+79}} + \frac{\eta_{C_2H_2}}{1+\frac{n_1}{n_2}0.354\frac{T+157}{T+220}}$$

H_2 %	C_2H_2 %	100°		80°		60°	
		$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1048	1048	1008	1008
84.87	15.13	1318	1293	1250	1237	1197	1183
77.88	22.12	1346	1333	1278	1274	1219	1218
69.01	30.99	1354	1360	1288	1298	1227	1239
51.28	48.72	1339	1366	1274	1301	1211	1239
29.71	70.29	1312	1335	1245	1270	1184	1206
0.00	100.00	1274	1274	1208	1208	1146	1146

H_2 %	C_2H_2 %	40°		20°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	965	965	924	924
84.87	15.13	1142	1128	1094	1073
77.88	22.12	1164	1160	1106	1100
69.01	30.99	1166	1179	1106	1116
51.28	48.72	1150	1176	1086	1112
29.71	70.29	1122	1145	1059	1079
0.00	100.00	1085	1085	1022	1022

Table 4. Viscosities of $H_2 \sim C_2H_6$. (Fig. 4.)

General formula: $$\eta = \frac{\eta_{H_2}}{1+\frac{n_2}{n_1}1.516\frac{T+243}{T+79}} + \frac{\eta_{C_2H_6}}{1+\frac{n_1}{n^2}0.328\frac{T+243}{T+280}}$$

H_2 %	C_2H_6 %	100°		80°		60°	
		$\eta\times10^7$		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1048	1048	1008	1008
83.69	16.31	1240	1230	1183	1176	1126	1122
66.51	33.49	1256	1260	1196	1199	1138	1141
50.84	49.16	1240	1251	1181	1188	1124	1129
37.16	62.84	1224	1232	1163	1169	1104	1110
0.00	100.00	1171	1171	1109	1109	1051	1051

Table 4.—(*Concluded*)

H_2 %	C_2H_6 %	40°		20°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	965	965	924	924
83.69	16.31	1071	1071	1013	1008
66.51	33.49	1077	1078	1013	1017
50.84	49.16	1062	1065	998	1001
37.16	62.84	1044	1046	980	981
0.00	100.00	991	991	928	928

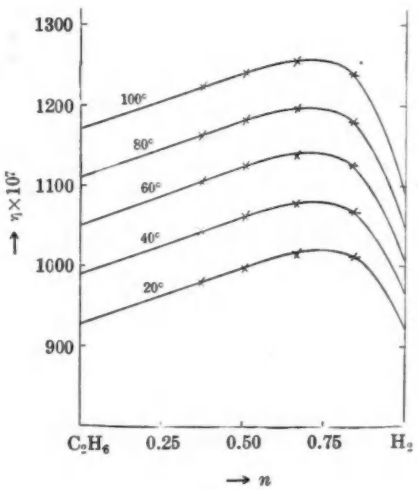


Fig. 4. $H_2 \sim C_2H_6$

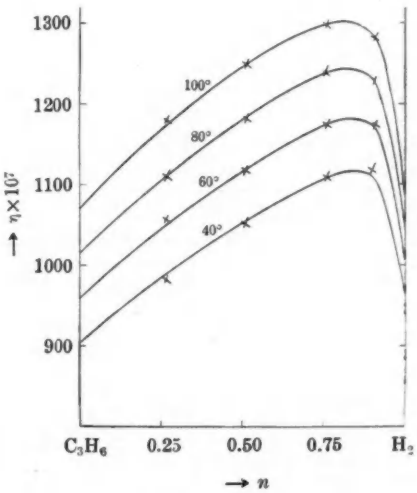


Fig. 5. $H_2 \sim C_3H_6$

Table 5. Viscosities of $H_2 \sim C_3H_6$. (Fig. 5.)

General formula: $\eta = \dfrac{\eta_{H_2}}{1+\dfrac{n_2}{n_1}1.746\dfrac{T+155}{T+79}} + \dfrac{\eta_{C_3H_6}}{1+\dfrac{n_1}{n_2}0.254\dfrac{T+155}{T+302}}$

H_2 %	C_3H_6 %	100°		80°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1090	1090	1048	1048
91.10	8.90	1284	1263	1231	1221
75.88	24.12	1296	1320	1240	1263
51.02	48.98	1250	1255	1181	1197
26.76	73.24	1181	1166	1110	1107
0.00	100.00	1070	1070	1016	1016

H_2 %	C_3H_6 %	60°		40°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1008	1008	965	965
91.10	8.90	1174	1160	1118	1106
75.88	24.12	1175	1203	1110	1142
51.02	48.98	1118	1136	1050	1073
26.76	73.24	1057	1047	983	987
0.00	100.00	960	960	904	904

Table 6. Viscosities of $CH_4 \sim C_2H_2$. (Fig. 6.)

General formula: $\eta = \dfrac{\eta_{CH_4}}{1+\dfrac{n_2}{n_1}1.135\dfrac{T+172}{T+170}} + \dfrac{\eta_{C_2H_2}}{1+\dfrac{n_1}{n_2}0.854\dfrac{T+172}{T+220}}$

CH_4 %	C_2H_2 %	100°		80°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1380	1380	1316	1316
75.11	24.89	1378	1379	1310	1316
49.53	50.47	1360	1359	1300	1294
24.72	75.28	1330	1320	1264	1257
0.00	100.00	1274	1274	1208	1208

Table 6.—(*Concluded*)

CH_4 %	C_2H_2 %	60°		40°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1255	1255	1191	1191
75.11	24.89	1250	1254	1186	1190
49.53	50.47	1236	1231	1171	1168
24.72	75.28	1200	1193	1138	1132
0.00	100.05	1146	1146	1085	1085

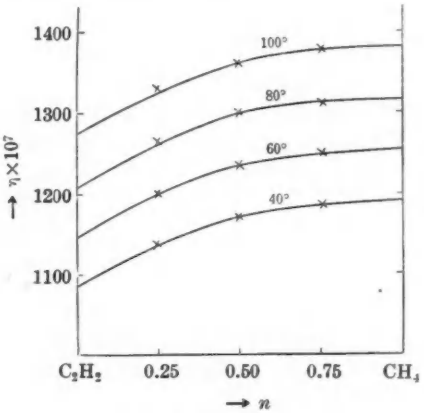


Fig. 6. $CH_4 \sim C_2H_2$

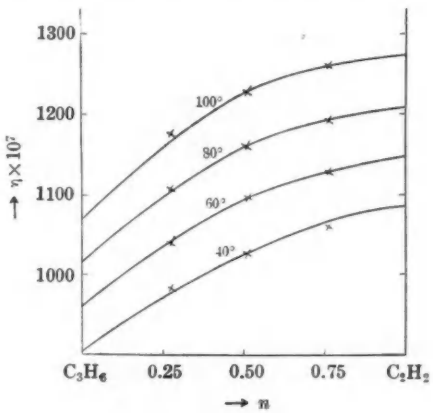


Fig. 7. $C_2H_2 \sim C_3H_6$

Table 7. Viscosities of $C_2H_2 \sim C_3H_6$. (Fig. 7.)

General formula: $$\eta = \frac{\eta_{C_2H_2}}{1+\frac{n_2}{n_1}1.165\frac{T+222}{T+220}} + \frac{\eta_{C_3H_6}}{1+\frac{n_1}{n_2}0.817\frac{T+222}{T+302}}$$

C_2H_2 %	C_3H_6 %	100°		80°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1274	1274	1208	1208
75.99	24.01	1261	1256	1192	1194
50.79	49.21	1228	1212	1160	1151
27.39	72.61	1176	1154	1108	1095
0.00	100.00	1070	1070	1016	1016

Table 7.—(*Concluded*)

C_2H_2 %	C_3H_6 %	60°		40°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1146	1146	1085	1085
75.99	24.01	1130	1132	1060	1071
50.79	49.21	1094	1080	1026	1031
27.39	72.61	1040	1036	982	977
0.00	100.00	960	960	904	904

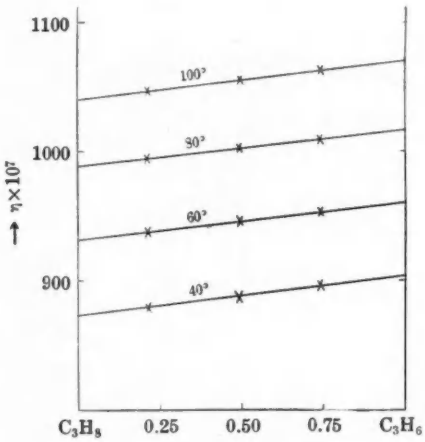


Fig. 8. C_3H_6~C_3H_8

Table 8. Viscosities of C_3H_6~C_3H_8. (Fig. 8.)

General formula: $$\eta = \frac{\eta_{C_3H_6}}{1+\frac{n_2}{n_1}1.008\frac{T+310}{T+302}} + \frac{\eta_{C_3H_8}}{1+\frac{n_1}{n_2}0.985\frac{T+310}{T+318}}$$

C_3H_6 %	C_3H_8 %	100°		80°	
		$\eta \times 10^7$		$\eta \times 10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	1070	1070	1016	1016
73.92	26.08	1062	1064	1009	1011
49.03	50.97	1056	1058	1001	1003
21.31	78.69	1046	1048	996	995
0.00	100.09	1040	1040	988	988

Table 8.—(*Concluded*)

C_3H_6 %	C_3H_8 %	60°		40°	
		$\eta\times10^7$		$\eta\times10^7$	
		Obs.	Calc.	Obs.	Calc.
100.00	0.00	960	960	904	904
73.92	26.08	952	954	896	897
49.03	50.97	946	947	886	890
21.31	78.69	940	939	878	881
0.00	100.00	932	932	873	873

As seen from the figure, the viscosities of the first four mixtures attain maximum values at definite compositions, which are about 20% of H_2 for the mixture $H_2\sim CH_4$ and about 70–80% of H_2 for the other three. The viscosity-composition curve of the mixture $C_3H_6\sim C_3H_8$ is quite linear.

Discussion.

Viscosity Formula for Binary Gaseous Mixture. The viscosity of gases depends on the diameter, the mass, and the attraction of the molecule, and further the mutual collision of the different gases must be considered in the case of a mixture and the theoretical treatment is difficult. As described above, many formulæ are proposed to express the viscosity of a gaseous mixture but they are derived almost empirically. Of those formulæ, that in which Kuenen's[8] consideration of the persistence of molecular velocity is introduced is somewhat more theoretical than the other. The experimental results will be examined first of all by this formula.

The viscosity η of a simple gas is given by

$$\eta = k m N \bar{u} \lambda f , \qquad (1)$$

where m is the mass, $\bar{u}$ the mean velocity, λ the mean free path of the molecule, N the number of molecules per unit volume, f the correction factor in consideration of the persistence of molecular velocity (1/0.797 in simple gas) and k a constant (0.499×0.797).

(8) J. P. Kuenen, "Die Eigenschaften der Gase," 111 (1919).

The viscosity of binary gaseous mixtures is given in a rather complicated formula. If the mean free path of the molecule in the mixture of the first type is λ_1' and the correction factor owing to the persistence in the mixture is f_1', there is obtained the following relations:

$$\eta = km_1n_1N\bar{u}_1\lambda_1'f_1' + km_2n_2N\bar{u}_2\lambda_2'f_2' , \qquad (2)$$

where n_1 and n_2 are mol fractions of two components. The mean free paths in a mixture are

$$\lambda_1' = \frac{1}{n_1N\pi S_1^2\sqrt{2}\left(1+\frac{C_1}{T}\right)+n_2N\pi S^2\sqrt{\frac{m_1+m_2}{m_2}}\left(1+\frac{C_{12}}{T}\right)} ,$$

$$\lambda_2' = \frac{1}{n_2N\pi S_2^2\sqrt{2}\left(1+\frac{C_2}{T}\right)+n_1N\pi S^2\sqrt{\frac{m_1+m_2}{m_1}}\left(1+\frac{C_{12}}{T}\right)} ,$$

where S_1 and S_2 are molecular diameters of two gases, S is a mean of these ($S = 1/2(S_1 + S_2)$), C_1 and C_2 are Sutherland's constants of two gases due to the attraction between the same molecules and C_{12} that between the different molecules.

According to Kuenen, the correction factors for a mixture, f', are as follows:

$$f_1' = \frac{1}{1-\frac{\sqrt{2}}{2}n_1N\pi S_1^2\left(1+\frac{C_1}{T}\right)\lambda_1'\times 0{\cdot}406-\frac{m_1}{m_1+m_2}n_2N\pi S^2\sqrt{\frac{m_1+m_2}{m_2}}\left(1+\frac{C_{12}}{T}\right)\lambda_1'\vartheta_1} ,$$

where $$\vartheta_1 = \frac{m_1}{2(m_1+m_2)}+\frac{1}{4}\frac{m_1^2}{\sqrt{m_2}(m_1+m_2)^{\frac{3}{2}}}\ln\frac{\sqrt{m_1+m_2}+\sqrt{m_2}}{\sqrt{m_1+m_2}-\sqrt{m_2}} ,$$

and analogous formulæ for f_2' and ϑ_2.

The viscosities of the components are also expressed by

$$\eta_1 = \frac{km_1\bar{u}_1}{\pi S_1^2\sqrt{2}\left(1+\frac{C_1}{T}\right)}\frac{1}{0{\cdot}797} , \qquad \eta_2 = \frac{km_2\bar{u}_2}{\pi S_2^2\sqrt{2}\left(1+\frac{C_2}{T}\right)}\frac{1}{0{\cdot}797} .$$

By inserting these values to equation (2), the viscosity of a mixture becomes

$$\eta = \frac{\eta_1}{1+\frac{n_2}{n_1}a_1} + \frac{\eta_2}{1+\frac{n_1}{n_2}a_2}, \qquad (3)$$

where $$a_1 = \left(\frac{S}{S_1}\right)^2 \sqrt{\frac{m_1+m_2}{2m_2}} \frac{1-\frac{m_1}{m_1+m_2}\vartheta_1}{0.797} \frac{T+C_{12}}{T+C_1},$$

$$a_2 = \left(\frac{S}{S_2}\right)^2 \sqrt{\frac{m_1+m_2}{2m_1}} \frac{1-\frac{m_2}{m_1+m_2}\vartheta_2}{0.797} \frac{T+C_{12}}{T+C_2}.$$

Sutherland's constant C_{12} is proportional to the potential energy of two different molecules, and the only coefficient in equation (3) that can not be determined directly, and is often considered to be a geometrical mean of C_1 and C_2. For almost all mixtures, whose viscosities have been measured by many authors, such calculations of this coefficient is inadequate to adapt the experiments. However, if we take a proper value for C_{12}, the results of observation can be expressed satisfactorily by equation (3). By using such values, viscosity formulæ for all mixtures can be obtained and these are given in Tables 3–8. The viscosity curve III in Fig. 9 is obtained by equation (3) by using C_{12} calculated as a geometrical mean and curve II by observed C_{12} computed empirically from the results of observation. The comparison of the calculated and the observed values of C_{12} are shown below in Table 9.

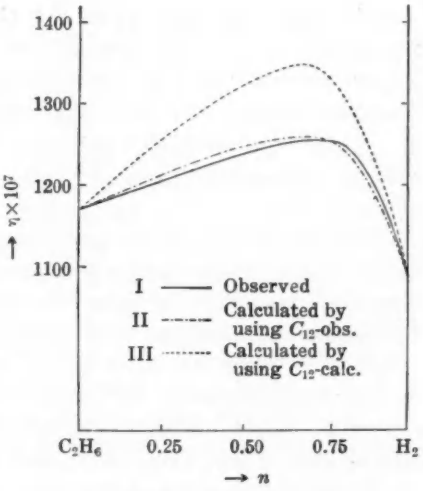


Fig. 9. H_2~C_2H_6 (100°C.)

Sutherland's Constant between Different Molecules. As described above, according to the classical theory, Sutherland's constant C_{12} has been considered to be a geometrical mean of C_1 and C_2. In 1928,

Schmick[9] reported that, when a dipole and a quadrupole molecules collide, the constant becomes smaller than the geometrical mean.

The potential energies between two dipole molecules, $E_{d_1d_2}$, between two quadrupole molecules, $E_{q_1q_2}$, and between a dipole and a quadrupole molecules, E_{dq}, are expressed as follows:

$$E_{d_1d_2} = -\frac{2}{3\sigma^6}\frac{\mu_1^2\mu_2^2}{kT}, \quad E_{q_1q_2} = -\frac{14}{5\sigma^{10}}\frac{\nu_1^2\nu_2^2}{kT}, \quad E_{dq} = -\frac{1}{\sigma^8}\frac{\mu^2\nu^2}{kT},$$

where μ and ν are the dipole and the quadrupole moments respectively, and σ the distance between two molecules.

Then for the same sort of molecules $E_{dd} = -\frac{2}{3\sigma^6}\frac{\mu^4}{kT}$ and $E_{qq} = -\frac{14}{5\sigma^{10}}\frac{\nu^4}{kT}$, hence $E_{dq} = 0.733\sqrt{E_{dd} \times E_{qq}}$. As Sutherland's constant is proportional to the potential energy between two molecules, this becomes

$$C_{12} = 0.733\sqrt{C_1 \times C_2}.$$

According to London's consideration[10] from the standpoint of wave mechanics, C_{12} is always smaller than the geometrical mean, and if it be larger, we can say that some forces other than van der Waals's, for example, valency force etc. must have acted between the molecules.

There is no method to determine C_{12} directly, but as described above, we can compute it inversely from viscosities of a mixture by using equation (3).

The values of C_{12} calculated for several paires by using viscosities obtained by the present author and other authors are given in Table 9. For nine mixtures out of thirty-two the values of C_{12} are equal to, and for thirteen larger than, the geometrical means. As the examples of a dipole and a quadrupole mixtures, C_{12}'s of $NH_3 \sim O_2$ and $NH_3 \sim N_2$ agree very well with Schmick's theory, but those of $NH_3 \sim C_2H_4$ and $NH_3 \sim H_2$ do not.

It is doubtful whether the values of C_{12} obtained by such a method are exactly proportional to the potential energies or not, and therefore, such calculations serve only to the estimation of the approximate values of the constant and it is dangerous to interpret the values of C_{12} larger than the geometrical mean by the consideration of London.

(9) H. Schmick, *Physik. Z.*, **29** (1928), 638.
(10) F. London, *Z. physik, Chem.*, B, **11** (1931), 222.

Table 9. Calculated Values of C_{12} and the Comparison with the Geometrical Means of C_1 and C_2.

Mixture	C_1	C_2	C_{12}	$\frac{C_{12}}{\sqrt{C_1C_2}}$	Mixture	C_1	C_2	C_{12}	$\frac{C_{12}}{\sqrt{C_1C_2}}$
NH_3~N_2	370	114	151	0.733	CH_4~C_2H_6	170	280	230	1.05
NH_3~O_2	370	137	165	0.733	H_2~He	79	76	82	1.05
He~Ne	76	56	62	0.80	N_2~NO	114	195	156	1.05
C_2H_4~O_2	259	137	160	0.85	H_2~NH_3	79	370	195	1.14
C_2H_4~C_3H_6	259	302	222	0.86	C_2H_4~CO_2	259	257	290	1.14
NH_3~C_2H_4	370	259	270	0.88	H_2~O_2	79	137	120	1.15
CH_4~C_2H_2	170	220	172	0.89	Ne~A	56	163	110	1.15
CO_2~C_3H_8	257	318	257	0.90	H_2~C_2H_2	79	220	159	1.19
O_2~CO_2	137	257	170	0.90	H_2~Ne	79	56	81	1.23
N_2~C_2H_4	114	259	160	0.93	CH_4~C_3H_8	170	318	305	1.31
CO~N_2	102	114	105	0.97	H_2~C_2H_4	79	259	200	1.40
H_2~C_3H_6	79	302	155	1.00	H_2~A	79	163	163	1.44
C_3H_6~C_3H_8	302	318	310	1.00	H_2~CH_4	79	170	169	1.46
N_2O~C_3H_8	314	318	316	1.00	H_2~CO_2	79	257	210	1.47
N_2~O_2	114	137	128	1.03	He~A	76	163	163	1.47
C_2H_6~C_3H_8	280	318	312	1.04	H_2~C_2H_6	79	280	243	1.63

The Conditions for the Occurrence of a Maximum Point. The conditions for the occurrence of a maximum point have been discussed by many authors in special cases. For example, Thomsen[11] reported that in the case of mixtures of two gases of nearly equal viscosities, maximum point occurs when the ratio of molecular weights is great; and Schmick[12] stated that, of mixtures of two gases, whose viscosities and molecular weights are nearly equal, those of a polar and a nonpolar molecules show maximum points.

We can not find any papers dealing with the conditions for the occurrence of a maximum point for a general case.

The general formula expressing the viscosity of a gaseous mixture is given by

$$\eta = \frac{\eta_1}{1+\frac{n_2}{n_1}a_1} + \frac{\eta_2}{1+\frac{n_1}{n_2}a_2}, \qquad (4)$$

(11) E. Thomsen, *Ann. Physik*, **36** (1911), 815.

(12) G. Jung and H. Schmick, *Z. physik. Chem.*, B, **7** (1930), 130.

and by introducing Kuenen's consideration into α_1 and α_2, we can derive the special form of this equation as given in equation (3). If we write $n_1 = n$, $n_2 = 1 - n$, then

$$\eta = \frac{\eta_1}{1+\frac{1-n}{n}\alpha_1} + \frac{\eta_2}{1+\frac{n}{1-n}\alpha_2} = \frac{n\eta_1}{n+(1-n)\alpha_1} + \frac{(1-n)\eta_2}{1-n+n\alpha_2} .$$

By differentiation we have

$$\frac{d\eta}{dn} = \frac{\alpha_1\eta_1\{(\alpha_2-1)n+1\}^2 - \alpha_2\eta_2\{(\alpha_1-1)n-\alpha_1\}^2}{(n+\alpha_1-n\alpha_1)^2(1-n+n\alpha_2)^2}$$

$$= A\left[\sqrt{\alpha_1\eta_1}\{\alpha_2+(1-n)\} - \sqrt{\alpha_2\eta_2}\{\alpha_1(1-n)+n\}\right], \quad (5)$$

where $$A \equiv \frac{\sqrt{\alpha_1\eta_1}\{\alpha_2+(1-n)\} + \sqrt{\alpha_2\eta_2}\{\alpha_1(1-n)+n\}}{(n+\alpha_1-n\alpha_1)^2(1-n+n\alpha_2)^2} .$$

If we equate $d\eta/dn$ to zero, we have the following equation, A being positive and not equal to zero.

$$\sqrt{\alpha_1\eta_1}\{\alpha_2+(1-n)\} - \sqrt{\alpha_2\eta_2}\{\alpha_1(1-n)+n\} = 0 .$$

Then the composition of the maximum or the minimum point, n_0, becomes

$$n_0 = \frac{\sqrt{\alpha_1}(\sqrt{\alpha_1\alpha_2\beta}-1)}{\sqrt{\alpha_1}(\alpha_2-1)+\sqrt{\alpha_2\beta}(\alpha_1-1)} = \frac{\sqrt{\alpha_1\alpha_2\beta}-1}{\sqrt{\alpha_1\alpha_2\beta}-1+\sqrt{\frac{\alpha_2}{\alpha_1}}(\sqrt{\alpha_1\alpha_2}-\sqrt{\beta})} , \quad (6)$$

where $\beta \equiv \eta_2/\eta_1$.

For the existence of a maximum or a minimum point, n_0 must be greater than nought and smaller than unity or as seen from equation (6), following conditions must be fulfilled:

$$\alpha_1\alpha_2 > \beta > \frac{1}{\alpha_1\alpha_2} \quad \text{or} \quad \alpha_1\alpha_2 < \beta < \frac{1}{\alpha_1\alpha_2} .$$

By inserting the values of n_0 given by (6), equation (5) becomes

$$\frac{d\eta}{dn} = A\sqrt{\alpha_1}\,\frac{n-n_0}{\sqrt{\alpha_1\alpha_2\beta}-1+\sqrt{\frac{\alpha_2}{\alpha_1}}(\sqrt{\alpha_2\alpha_1}-\sqrt{\beta})} . \quad (7)$$

where $A\sqrt{\alpha_1}$ is positive if $0 < n_0 < 1$.

Then if $\alpha_1\alpha_2 > \beta > \frac{1}{\alpha_1\alpha_2}$, the demoninator of equation (7) becomes positive and

$$\frac{d\eta}{dn} < 0 \qquad \text{when} \quad n < n_0 ,$$

$$\frac{d\eta}{dn} > 0 \qquad \text{when} \quad n > n_0 ,$$

hence η becomes minimum when $n = n_0$.

Next, if $\alpha_1\alpha_2 < \beta < \frac{1}{\alpha_1\alpha_2}$, the denominator of equation (7) becomes negative and

$$\frac{d\eta}{dn} > 0 \qquad \text{when} \quad n < n_0 ,$$

$$\frac{d\eta}{dn} < 0 \qquad \text{when} \quad n > n_0 ,$$

hence η becomes maximum when $n = n_0$.

By summarising,

$$\left.\begin{array}{lll} \text{when} \quad \alpha_1\alpha_2 > \beta > \dfrac{1}{\alpha_1\alpha_2} & \text{viscosity shows a} & \text{minimum,} \\ \alpha_1\alpha_2 < \beta < \dfrac{1}{\alpha_1\alpha_2} & ,, \qquad ,, & \text{a maximum,} \\ \left.\begin{array}{l} \dfrac{1}{\beta} < \alpha_1\alpha_2 < \beta \\ \text{or} \quad \beta < \alpha_1\alpha_2 < \dfrac{1}{\beta} \end{array}\right\} & ,, \qquad ,, & \text{neither.} \end{array}\right\} \qquad (8)$$

This relations hold in the general formula of binary mixtures whatever the values of α_1 and α_2 may be, but in order to examine numerically by examples, let us insert the values given in (3) to α_1 and α_2. If we write $m_2/m_1 \equiv \mu$, $S_2/S_1 \equiv a$, $\dfrac{1+\dfrac{C_2}{T}}{1+\dfrac{C_1}{T}} \equiv \nu$ and assume $\dfrac{(T+C_{12})^2}{(T+C_1)(T+C_2)} = 1$, then

$$\left.\begin{aligned} \alpha_1\alpha_2\beta &= \left(\frac{1+a}{2a}\right)^4 \frac{B}{\nu} , \\ \frac{\alpha_1\alpha_2}{\beta} &= \left(\frac{1+a}{2}\right)^4 \frac{B\nu}{\mu} , \end{aligned}\right\} \qquad (9)$$

where $B = \frac{1+\mu}{1.27}\left(1-\frac{\vartheta_1}{1+\mu}\right)\left(1-\frac{\vartheta_2}{1+\mu}\mu\right)$.

Above assumption is not rigorous, but, if C_{12} lies between C_1 and C_2, $(T+C_{12})^2/(T+C_1)(T+C_2)$ is not very far from unity.

The results of calculations of $\alpha_1\alpha_2\beta$ and $\alpha_1\alpha_2/\beta$ at 0°C. by formula (8) for fifty-five kinds of gaseous mixtures are tabulated in Table 10, the components of mixtures being selected as $m_2>m_1$.

Table 10.

(1) Mixtures showing a maximum.

Mixture	$\alpha_1\alpha_2\beta$	$\frac{\alpha_1\alpha_2}{\beta}$	Observers
H_2~CH_4	0.740	0.526	Adzumi, Graham[13], Trautz and Sorg[28].
H_2~C_2H_2	0.574	0.485	Adzumi.
H_2~C_2H_4	0.537	0.498	Thomsen[11], Trautz and Stauf[22].
H_2~C_2H_6	0.499	0.517	Adzumi.
H_2~C_3H_6	0.416	0.514	Adzumi.
H_2~C_3H_8	0.385	0.510	
H_2~NH_3	0.622	0.574	Thomsen[11], Trautz and Heberling[29].
H_2~CO_2	0.675	0.242	Graham[13], Puluj[2] Thomsen[11], Breitenbach[14], Trautz and Kurz[27].
H_2~SO_2	0.433	0.265	Trautz and Weizel[18].
H_2~NO	0.890	0.245	Graham[13].
H_2~N_2O	0.646	0.249	Graham[13], Trautz and Kurz[27].
H_2~HCl	0.662	0.279	Trautz and Narath[19].
H_2~Cl_2	0.479	0.243	Thomsen[11].
He~A	0.718	0.460	Tänzler[16], Trautz and Kipphan[23], Trautz and Binkele[25].
He~Kr	0.552	0.374	Nasini and Rossi[20].
*CH_4~NH_3	0.852	1.120	Jung and Schmick[12].
*NH_3~C_2H_4	0.990	1.004	Thomsen[11], Trautz and Heberling[29].

(13) Graham, *Trans. Roy. Soc.* (London), A, **136** (1846), 662.
(14) Breitenbach, *Wied. Ann.*, **67** (1899), 803.
(15) K. Kleint, *Verh. deut. phys. Ges.*, **7** (1905), 146.
(16) P. Tänzler, *Verh. deut. phys. Ges.*, **8** (1906), 221.
(17) A. Gille, *Ann. Physik*, **48** (1915), 799.
(18) M. Trautz and W. Weizel, *Ann. Physik*, **78** (1925), 305.
(19) M. Trautz and A. Narath, *ibid.*, **79** (1926), 637.
(20) Nasini and Rossi, *Gazz. chim. ital.*, **58** (1928), 433.
(21) M. Trautz and P. B. Baumann, *Ann. Physik*, (V), **2** (1929), 733.

Table 10.—(*Continued*)

(2) Mixtures showing no maximum.

Mixture	$\alpha_1\alpha_2\beta$	$\frac{\alpha_1\alpha_1}{\beta}$	Observers
* H_2~CO	0.928	0.260	Graham[13], Tratz and Baumann[21].
H_2~O_2	1.018	0.205	Kleint[15], Graham[13], Trautz and Melster[26].
* H_2~N_2	0.960	0.254	Graham[13], Kleint[15], Trautz and Baumann[21].
* H_2~Air	0.954	0.247	Graham[13].
H_2~He	2.110	0.308	Gille[17], Trauz and Kipphan[23], Trauz and Baumann[21].
H_2~A	1.110	0.152	Trautz and Ludewigs[24], Trauz and Binkele[25].
H_2~Ne	1.901	0.157	Trautz and Binkele[25].
He~Ne	1.20	0.455	Trautz and Kipphan[23].
Ne~A	0.744	1.260	Trautz and Kipphan[23], Trauz and Binkele[15].
NH_3~N_2	1.694	0.521	Thomsen[11], Trautz and Heberling[29].
NH_3~O_2	1.435	0.566	Thomsen[11], Trautz and Heberling[29].
NH_3~Air	1.82	0.520	Jung and Schmick[12].
NH_3~CO_2	1.435	0.566	Thomsen[11].
NH_3~Cl_2	1.08	0.459	Thomsen[11].
Air~CO_2	0.837	1.160	Jung and Schmick[12].
Air~HCl	0.770	1.212	
Air~H_2S	0.657	1.456	
CO~N_2	1.032	0.97	Trautz and Melster[26].
CO_2~N_2O	0.963	1.039	Trautz and Kurz[27].
CO_2~SO_2	0.773	1.266	Jung and Schmick[12].
O_2~CO_2	0.745	1.333	Graham[13].
CO~O_2	1.20	0.837	Graham[13], Trautz and Melster[26].
N_2~O_2	1.16	0.817	Graham[13], Kleint[15], Trautz and Melster[26].
N_2~NO	0.978	1.055	Trautz and Gabriel[30].

(22) M. Trautz and F. W. Stauf, *Ann. Physik*, (V), **2** (1929), 737.
(23) M. Trautz and K. F. Kipphan, *ibid.*, (V), **2** (1929), 743.
(24) M. Trautz and W. Ludewigs, *ibid.*, (V), **3** (1929), 409.
(25) M. Trautz and H. E. Binkele, *ibid.*, (V), **5** (1930), 561.
(26) M. Trautz and A. Melster, *ibid.*, (V), **7** (1930), 409.
(27) M. Trautz and F. Kurz, *ibid.*, (V), **9** (1931), 981.
(28) M. Trautz and K. G. Sorg, *ibid.*, (V), **10** (1931), 81.
(29) M. Trautz and R. Heberling, *ibid.*, (V), **10** (1931), 155.
(30) M. Trautz and E. Gabriel, *ibid.*, (V), **11** (1931), 606.

Table 10.—(*Concluded*)

Mixture	$\alpha_1\alpha_2\beta$	$\frac{\alpha_1\alpha_2}{\beta}$	Observers
CH_4~O_2	1.84	0.463	Graham[12].
CH_4~C_2H_2	0.900	1.074	Adzumi.
CH_4~C_2H_6	0.793	1.180	Trautz and Sorg[28].
CH_4~C_3H_8	0.656	1.258	Trautz and Sorg[28].
C_2H_2~C_3H_6	0.808	1.20	Adzumi.
N_2~C_2H_4	0.539	1.895	Trautz and Melster[26].
CO~C_2H_4	0.556	1.833	Trautz and Melster[26].
C_2H_4~O_2	2.27	0.496	Trautz and Melster[26].
C_2H_4~Air	1.92	0.524	Breitenbach[14].
C_2H_4~CO_2	1.565	0.603	
C_2H_6~C_3H_8	0.920	1.10	Trautz and Sorg[28].
C_3H_6~C_3H_8	0.945	1.02	Adzumi.
C_3H_8~N_2O	1.945	0.564	Trautz and Kurz[27].
C_3H_8~CO_2	2.01	0.538	Trauz and Kurz[27].

As seen from Table 10, all mixtures showing a maximum have the values of $\alpha_1\alpha_2\beta$ and $\alpha_1\alpha_2/\beta$ always smaller than unity and in the case of mixtures showing no maximum the values are either $\left.\begin{matrix}\alpha_1\alpha_2\beta<1\\ \alpha_1\alpha_2>\beta\end{matrix}\right\}$ or $\left.\begin{matrix}\alpha_1\alpha_2\beta<1\\ \alpha_1\alpha_2<\beta\end{matrix}\right\}$, thus the conditions (8) are satisfied excepting a few mixtures prefixed by an asterisk which have values only a little different from unity, but by inserting the correct values to C_{12}, all of these will perhaps satisfy the conditions (8).

Fig. 10 is a graphical interpretation of the conditions (8). The boundary curves between the region in which a maximum point occurs and that in which a maximum point does not occur are

$$\left.\begin{aligned} &\alpha_1\alpha_2\beta = 1 \quad \text{or} \quad \alpha = \frac{1}{2\sqrt[4]{\frac{\nu}{B}}-1},\\ &\text{and} \quad \alpha_1\alpha_2 = \beta \quad \text{or} \quad \alpha = 2\sqrt[4]{\frac{\mu}{B\nu}}-1. \end{aligned}\right\} \tag{10}$$

In Fig. 10 μ is taken as ordinate and α as abscissa when ν equals to 0.5, 1.0, and 2.0, and the shaded part between two curves of $\alpha_1\alpha_2\beta = 1$ and $\alpha_1\alpha_2 = \beta$ is the region of a maximum or a minimum point.

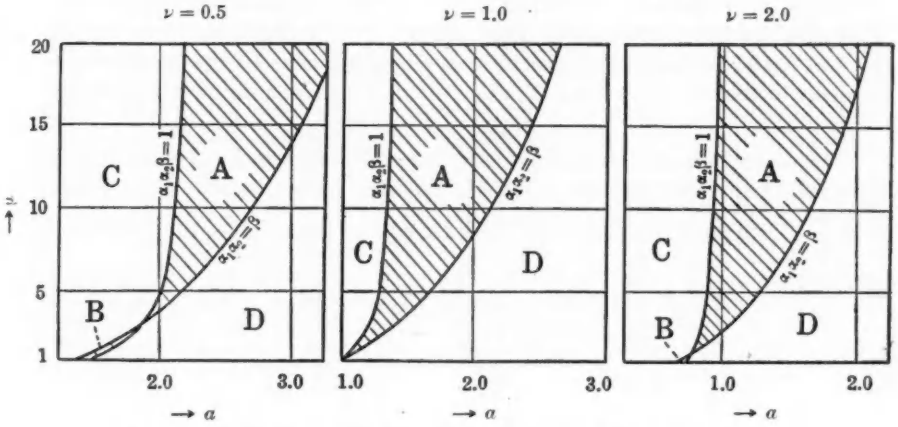


Fig. 10. Graphical Interpretation of the Conditions for the Occurrence of a Max. or a Min. Point. $\left(\mu=\frac{m_2}{m_1},\ \alpha=\frac{S_2}{S_1},\ \nu=\frac{T+C_2}{T+C_1}\right)$.

(A) is a region of $\left.\begin{matrix}\alpha_1\alpha_2\beta<1\\ \alpha_1\alpha_2<\beta\end{matrix}\right\}$ and in which a maximum point occurs,

(B) ,, $\left.\begin{matrix}\alpha_1\alpha_2\beta>1\\ \alpha_1\alpha_2>\beta\end{matrix}\right\}$,, a minimum ,, ,

(C) ,, $\left.\begin{matrix}\alpha_1\alpha_2\beta>1\\ \alpha_1\alpha_2<\beta\end{matrix}\right\}$,, neither max. nor min. occurs,

(D) ,, $\left.\begin{matrix}\alpha_1\alpha_2\beta<1\\ \alpha_1\alpha_2>\beta\end{matrix}\right\}$,, ,, ,, ,

The mean free path of a molecule in a mixture is different from that of a simple molecule on account of the mutual collision between the different molecules, sometimes greater and sometimes smaller depending on the other molecule, and consequently the viscosity of the mixture is much complicated. It is a special case that the viscosity of a mixture follows the additive law, that is a case when $\alpha_1=\alpha_2=1$. As seen from Fig. 8, for example, the viscosity of $C_3H_6\sim C_3H_8$ is almost additive, because the molecular weights, the molecular diameters and Sutherland's constants of C_3H_6 and C_3H_8 are nearly equal respectively and then $\alpha_1\fallingdotseq\alpha_2\fallingdotseq1$. In general, the viscosity curve deviates from a straight line, and by the mutual combination between α, μ, and ν, sometimes a maximum point occurs as easily seen from Fig. 10.

The existence of a minimum point is not improbable though any example has not been found. The area of (B) in Fig. 10 is very small, so that the probability of the occurrence of such a case by the combination of a few constants is very small, and when $C_1 = C_2$ a minimum point does not exist.

In order to know the relation between the conditions for the occurrence of a maximum point and the ratios of viscosities of two gases, β, we insert $a = \frac{\sqrt[4]{\mu}}{\sqrt{\beta\nu}}$ to equation (10), then we have as the formulæ of the boundary curves:

$$\left.\begin{aligned} &\beta = \frac{\sqrt{\mu}}{\nu}\left(2\sqrt[4]{\frac{\nu}{B}} - 1\right)^2, \\ \text{and} \qquad &\beta = \frac{\sqrt{\mu}}{\left(2\sqrt[4]{\frac{\mu}{B\nu}} - 1\right)^2 \nu}. \end{aligned}\right\} \tag{11}$$

As similarly as equation (10), this is represented graphically in Fig. 11, β being taken as abscissa. The shaded part indicates also the region of a maximum point and the greater the ratio μ is the wider this region becomes, and therefore the maximum point is very apt to occur if the ratio of two molecular weights is great. But if the ratio of two viscosities is great, the maximum point occurs only when the ratio of molecular weights is very great.

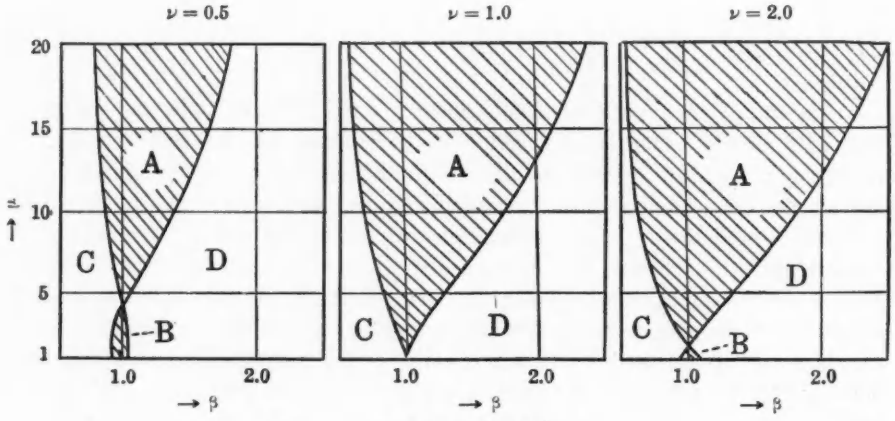


Fig. 11. $\left(\beta = \frac{\nu_2}{\nu_1}\right)$.

The above discussions are based on equation (3), in which the factor of the persistence of molecular velocity is introduced. Next, let us consider the case when the persistence of velocity is neglected, then α_1 and α_2 become:

$$\alpha_1 = \left(\frac{S}{S_1}\right)^2 \sqrt{\frac{m_1+m_2}{2m_2}}\,\frac{T+C_{12}}{T+C_1},$$

$$\alpha_2 = \left(\frac{S}{S_2}\right)^2 \sqrt{\frac{m_1+m_2}{2m_1}}\,\frac{T+C_{12}}{T+C_2}.$$

By inserting these values, $\alpha_1\alpha_2\beta$ and $\alpha_1\alpha_2/\beta$ become the same formulæ as (9), excepting that B has the following value:

$$B = \frac{1+\mu}{2}.$$

As similarly as equation (10), this relation is represented graphically in Fig. 12. As seen from the figure, not only the shape of the shaped part is different from Fig. 10, but also the relative position of two curves

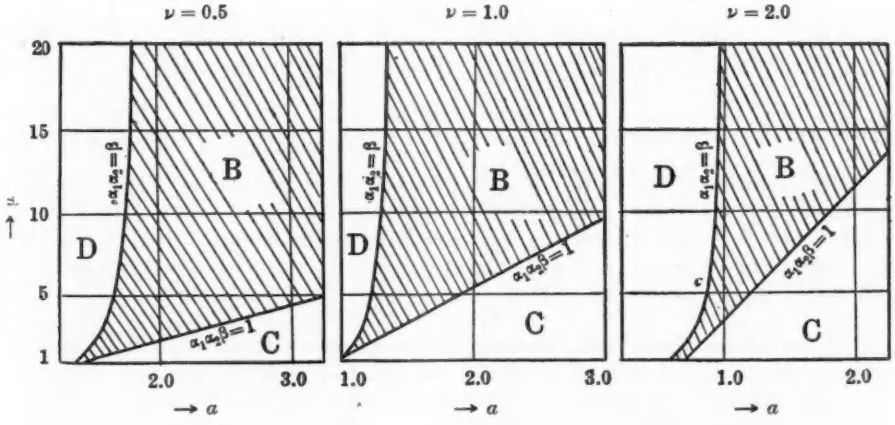


Fig. 12.

of $\alpha_1\alpha_2\beta = 1$ and $\alpha_1\alpha_2 = \beta$ is inverted, and consequently the shaded part in Fig. 12 corresponds to the region of a minimum point and that of a maximum point does not exist. This is of course contrary to the fact. Namely, the consideration of the persistence of velocity is absolutely necessary to explain the occurrence of a maximum point.

On the Displacement of the Composition of the Maximum Point. The composition of the maximum point displaces with the change of temperature. The displacements of four mixtures are given in Table 11. As seen from the table, the maximum point displaces to the lower concentration of hydrogen with the rise of temperature.

Table 11. The Compositions (H_2 %) of Maximum Points.

t°C	n_0			
	H_2~CH_4	H_2~C_2H_2	H_2~C_2H_6	H_2~C_3H_6
100	0.146	0.692	0.691	0.810
80	—	0.703	0.703	0.822
60	0.180	0.720	0.718	0.840
40	—	0.731	0.730	0.853
20	0.214	0.746	0.741	—

The composition of the maximum point is by (6)

$$n_0 = \frac{\sqrt{\alpha_1\alpha_2\beta}-1}{\sqrt{\alpha_1\alpha_2\beta}-1+\sqrt{\frac{\alpha_2}{\alpha_1}}(\sqrt{\alpha_1\alpha_2}-\sqrt{\beta})}.$$

This formula contains α, μ, ν, and $\frac{(T+C_{12})^2}{(T+C_1)(T+C_2)}$ and as the first three is independent of temperature, the displacement of n_0 is due to the change of the term of Sutherland's constant. If $C_1 = C_2$, perhaps C_{12} being also the same, this term vanishes and n_0 becomes independent of temperature. Therefore, the displacement of n_0 is due to the difference of Sutherland's constants of two gases.

The Mean Free Paths of Gas Molecules in a Mixture. The mean free paths of a molecule in a simple gas and in a mixture are expressed by the following formulæ, the persistence of molecular velocity being taken into consideration.

In a simple gas: $$\lambda_{01}^{(31)} = \frac{1}{N\pi S_1^2\sqrt{2}\left(1+\frac{C_1}{T}\right)\times 0.797}$$

(31) The suffix o is used to indicate that the persistence of velocity is considered and to distinguish from the mean free path without consideration of it used in equation (3).

$$\text{or} \qquad \lambda_{02} = \frac{1}{N\pi S_2^2 \sqrt{2}\left(1+\frac{C_2}{T}\right)\times 0.797}$$

$$\text{and in a mixture:} \qquad \left.\begin{aligned} \lambda'_{01} &= \frac{\lambda_{01}}{n_1+n_2\alpha_1}\ , \\ \lambda'_{02} &= \frac{\lambda_{02}}{n_2+n_1\alpha_2}\ , \end{aligned}\right\} \qquad (12)$$

where α_1 and α_2 have the same values as given in (3).

λ'_0's at 0°C. and 1 atm. pressure calculated by (12) for seven mixtures, whose viscosities have been measured by the present author, are given in Table 12, in which the value in brackets is the path when extremely small quantities of a gas are in another.

Table 12.

$H_2 \sim CH_4$

$H_2\,(n_1)$	$\lambda'_{01}\times 10^8$	$CH_4\,(n_2)$	$\lambda'_{02}\times 10^8$
1.00	1445	1.00	615
0.75	1244	0.75	708
0.50	1093	0.50	834
0.25	977	0.25	1010
0.00	(880)	0.00	(1288)

$H_2 \sim C_2H_2$

$H_2\,(n_1)$	$\lambda'_{01}\times 10^8$	$C_2H_2\,(n_2)$	$\lambda'_{02}\times 10^8$
1.00	1445	1.00	439
0.75	1272	0.75	530
0.50	1030	0.50	670
0.25	902	0.25	910
0.00	(801)	0.00	(1420)

$H_2 \sim C_2H_6$

$H_2\,(n_1)$	$\lambda'_{01}\times 10^8$	$C_2H_6\,(n_2)$	$\lambda'_{02}\times 10^8$
1.00	1445	1.00	370
0.75	1106	0.75	447
0.50	898	0.50	567
0.25	755	0.25	772
0.00	(651)	0.00	(1209)

$H_2 \sim C_3H_6$

$H_2\,(n_1)$	$\lambda'_{01}\times 10^8$	$C_3H_6\,(n_2)$	$\lambda'_{02}\times 10^8$
1.00	1445	1.00	285
0.75	1123	0.75	358
0.50	927	0.50	479
0.25	786	0.25	728
0.00	(682)	0.00	(1506)

$CH_4 \sim C_2H_2$

$CH_4\,(n_1)$	$\lambda'_{01}\times 10^8$	$C_2H_2\,(n_2)$	$\lambda'_{02}\times 10^8$
1.00	615	1.00	439
0.75	594	0.75	466
0.50	574	0.50	496
0.25	556	0.25	530
0.00	(540)	0.00	(570)

$C_2H_2 \sim C_3H_6$

$C_2H_2\,(n_1)$	$\lambda'_{01}\times 10^8$	$C_3H_6\,(n_2)$	$\lambda'_{02}\times 10^8$
1.00	439	1.00	285
0.75	422	0.75	308
0.50	405	0.50	335
0.25	389	0.25	367
0.00	(375)	0.00	(406)

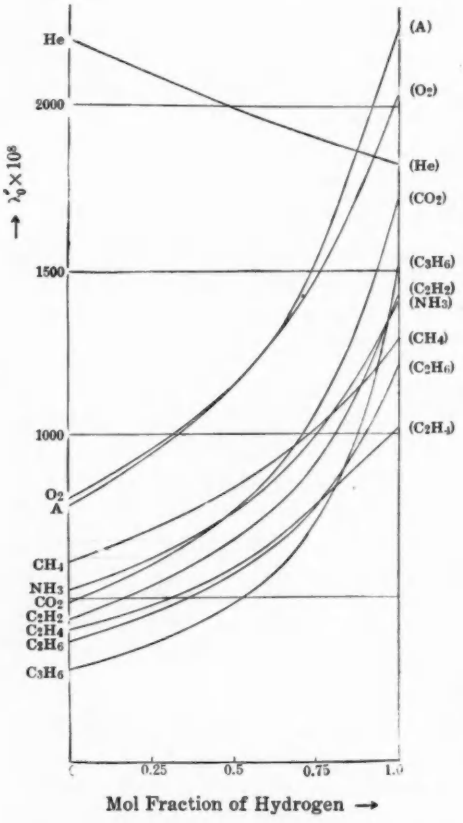


Fig. 13. The Change of the Mean Free Paths of Molecules in Hydrogen.

Table 12.—(*Concluded*)

$C_3H_6 \sim C_3H_8$

C_3H_6 (n_1)	$\lambda'_{01}\times10^8$	C_3H_8 (n_2)	$\lambda'_{02}\times10^8$
1.00	285	1.00	270
0.75	283.5	0.75	272
0.50	282	0.50	274
0.25	280	0.25	276
0.00	(279)	0.00	(278)

$NH_3 \sim N_2$

NH_3 (n_1)	$\lambda'_{01}\times10^8$	N_2 (n_2)	$\lambda'_{02}\times10^8$
1.00	522	1.00	751
0.75	558	0.75	754
0.50	600	0.50	756
0.25	648	0.25	759
0.00	(704)	0.00	(762)

$C_2H_6 \sim C_3H_8$

C_2H_6 (n_1)	$\lambda'_{01}\times10^8$	C_3H_8 (n_2)	$\lambda'_{01}\times10^8$
1.00	370	1.00	270
0.75	380	0.75	260
0.50	389	0.50	250
0.25	400	0.25	241
0.00	(412)	0.00	(233)

The change of the mean free paths of many gases due to the mixing of hydrogen are represented graphically in Fig. 13.

Generally the smaller mean free paths increases in the presence of molecules with the greater mean free paths and vice versa, excepting the case of $N_2 \sim NH_3$ and $C_2H_6 \sim C_3H_8$ whose change of paths are also given in Fig. 12.

Summary.

(1) Viscosities of six following simple gases and seven binary gaseous mixtures have been measured by the transpiration method over the temperature range between 20° and 100°C.

H_2, CH_4, C_2H_2, C_3H_6, C_3H_8, $H_2 \sim CH_4$, $H_2 \sim C_2H_2$, $H_2 \sim C_2H_6$, $H_2 \sim C_3H_6$, $CH_4 \sim C_2H_2$, $C_2H_2 \sim C_3H_6$, $C_3H_6 \sim C_3H_8$.

(2) The viscosities of the first four mixtures attain maximum values at definite compositions, which are about 20% of H_2 for the mixture $H_2 \sim CH_4$ and about 70–80% of H_2 for the other three.

(3) Of several formulæ proposed to express the viscosity of gaseous mixtures, that in which Kuenen's consideration of the persistence of molecular velocity is introduced seems to be the most appropriate. The results of observation can be expressed satisfactorily by that formula, if we take a proper value for one of Sutherland's constants which is due to the attraction between the different molecules and can not be determined directly.

(4) The theoretical consideration of this Sutherland's constant by Schmick and London have been examined by thirty-two examples.

(5) The conditions for the occurrence of a maximum and a minimum points have been obtained from the discussion of the viscosity formula and these have been examined numerically for fifty-five mixtures, and found to be always correct except for only five cases.

The viscosity-composition curve deviates in general from a straight line. The deviation depends on the ratios of molecular weights, molecular diameters, and Sutherland's constants of two component gases. Especially the maximum point is very liable to occur if the ratio of two molecular weights is great.

(6) It has been shown that, if the persistence of molecular velocity be neglected, the condition for the occurrence of a maximum point cannot be fulfilled and the consideration of the persistence is absolutely necessary to explain this point.

(7) The composition of the maximum point displaces with the change of temperature. This is found to be due to the difference of Sutherland's constants of two component gases.

(8) The mean free path of each component gas has been calculated. Generally the smaller mean free paths increases in the presence of

molecules with the greater mean free paths and vice versa, excepting a few cases.

In conclusion, the author wishes to express his sincere thanks to Prof. M. Katayama for his kind guidance throughout the present study.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

On a New Unsaturated Fatty Acid, $C_{10}H_{18}O_2$, Present in the Oil of *Rindera obtusiloda*.

By Saburo KOMORI and Sei-ichi UENO.

(Received April 30th, 1937.)

The oil (5 kg.), extracted with ether from the nuts of *Rindera obtusiloda* grown in Korea, was saponified, decomposed, and the mixed fatty acids thus obtained were subjected to fractional distillation under a reduced pressure of 13 mm. A fraction up to 160° was taken, and, after the removal of the unsaponifiable matter, was again fractionally distilled. The low boiling portion was separated into unsaturated and saturated acids by the Ba-salt-ether method. The unsaturated acid portion was fractionally distilled once more, and finally 2.94 g. of the unsaturated acid possessing the following values were obtained: neutralisation value 327.5, iodine value 128.5.

The unsaturated acid thus obtained was hydrogenated, and the product recrystallized from 70% alcohol had m.p. 30.5–30.9° and no depression was observed in admixture with pure capric acid. Hence it was recognized that the original acid was a straight chain compound with 10 carbon atoms. Further this unsaturated acid was converted into methyl ester and the methyl ester, subjected to oxidation and splitting with powdered potassium permanganate in acetone solution, yielded succinic and caproic acids, thus establishing that the original unsaturated fatty acid has the constitution $CH_3(CH_2)_4CH{:}CH(CH_2)_2COOH$. No compound with this structure is found in literature and the authors propose the name "obtusilic acid" for it.

Department of Chemical Technology,
Faculty of Engineering, Imperial University of Osaka.

Adsorption of Solvent Vapour by the Solute Crystal.

By Ituro UHARA and Morizumi NAKAMURA.

(Received April 13th, 1937.)

Lumping of Powder of the Soluble Substance. Lumping of the powder of cane sugar or common salt in the wet air is usually attributed to deliquescence, but this explanation is not necessarily correct. When the dry powder of pure substances (the humidity of the vapour from the saturated aqueous solution being h_s) containing no deliquescent impurities is exposed to the air of the humidity h, lumping is observed even when h is less than h_s in a few minutes and sometimes even in under one minute, if h is larger than about two-third of h_s in the cases of fairly soluble salts.

Table.

Powder (magnitude)	h_s %	h % of air bubbled through H_2SO_4 or the saturated solution of		Lumping of powder
NaCl (0.1—0.3 mm.)	76.0 (25°)	0 (25°)	conc. H_2SO_4	not observed (−)
		36.9 ,,	50 % ,,	− ?
		46.2 ,,	45 % ,,	+
KBr (0.1—0.3 mm.)	84 (20°)	55.5 (20°)	$Ca(NO_3)_2 \cdot 4H_2O$	a little
		63.4 ,,	NH_4NO_3	+
		77.9 ,,	NaCl	strongly +
		79.4 ,,	NH_4Cl	strongly +
		81.0 ,,	$(NH_4)_2SO_4$	strongly +
Tartaric acid (0.1—1 mm.)	86 (26.18°)	0 (25°)	conc. H_2SO_4	−
		62.1 ,,	NH_4NO_3	?
		76.0 ,,	NaCl	+
		79.5 ,,	NH_4Cl	strongly +
Cane sugar (0.2—0.8 mm.)	81.2—79.5[2] (25°)	76.0 ,,	NaCl	+

As the lump maintains its form on quiet heating, this phenomenon is not due to the cohesion of condensed water. The regional formation of

(1) NaCl was heated for several hours at 400°.

(2) This value is between that of ammonium sulphate and ammonium chloride and determined by observing deliquescence putting in one vessel.

the saturated solution and recrystallization of particles through this liquid layer is probable, as h_s is depressed due to the incomplete surface structure of the powder, but this not considered the most important cause, for lumping is also observed when h is less than h_s in the case of the following samples of which surface structure is fairly normal:

(1) powder of sodium chloride is put in the saturated solution for hours, filtered, washed with alcohol, and dried without touching each other. After putting in the air of $h = 60\%$ for several hours water adsorbed is driven away by heating quietly.

(2) powder of sodium chloride or potassium bromide, which had undergone the repeated adsorption and desorption of water vapour and is supposed to have lost the abnormally active part at the crystal surface by recrystallization if the liquid layer is formed.

(3) powder of these salts heated for hours at 200–400° where the motion of ions is violent enough to rearrange the irregular surface.[3]

Adsorption of the Solvent Vapour on the Solute Crystal. After repeated adsorption and desorption of water vapour, powder of potassium bromide (0.1–0.3 mm., 47.7816 g.) is put in an evacuated small desiccator with the saturated solution of a salt of which h_s is known and weighed after two hours (20.8°).

The dimension of each particle of a part of the well mixed sample is measured under the microscope and the surface area (0.563 cm.^{2}

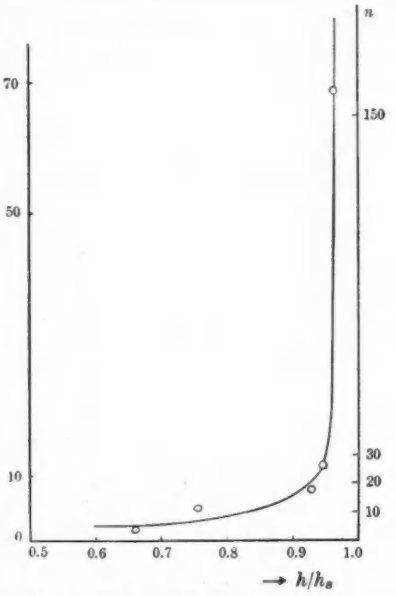


Fig. 1. Water Adsorbed by 47.7816 g. n-Molecular Layer of KBr Powder at 20.8°.

(3) According to Tammann, *Z. anorg. Chem.*, **126** (1923), 119, powders of various substances lump even at temperatures considerably lower than the melting point (NaCl 260°, cane sugar 69° ..), and this is attributed to the recrystalization due to the increased vibration of ions or molecules in the crystal. As our results were obtained at common temperature, they can not be explained in this way.

for 340 particles) and weight (density = 2.756, volume = 1.40×10^{-3}c.c., $\therefore 3.85 \times 10^{-3}$g.) are computed as the rectangular parallelopiped and the total area is 7.0×10^{3}cm.^{2}[4] The thickness of the adsorption layer is calculated assuming the real surface area is twice the geometrically determined value and is shown in Fig. 1. (monomolecular layer corresponds 3.1×10^{-8}g. H_2O/cm.^{2}) Only little is known about the adsorption of the solvent vapour on the solute crystal. Durau[5] studied the adsorption of water vapour by sodium chloride powder by measuring the pressure and obtained the analogous curve with that in Fig. 1, but he described that this method does not give exact results for soluble solids.

Electric Conductance and Electrolysis in the Adsorbed Layer. A crystal of potassium bromide is heated to 400–500° and is cooled in the apparatus shown in Fig. 2 in the current of dry air, then the surface con-

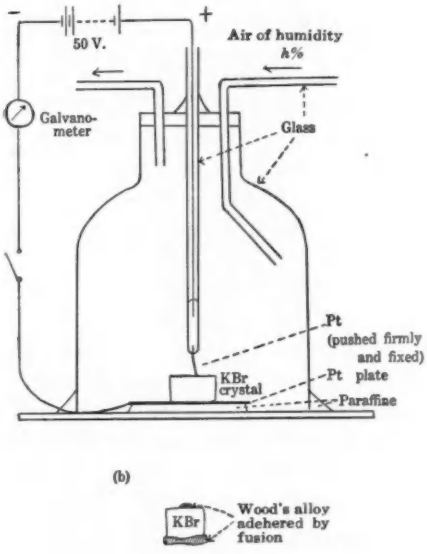


Fig. 2.

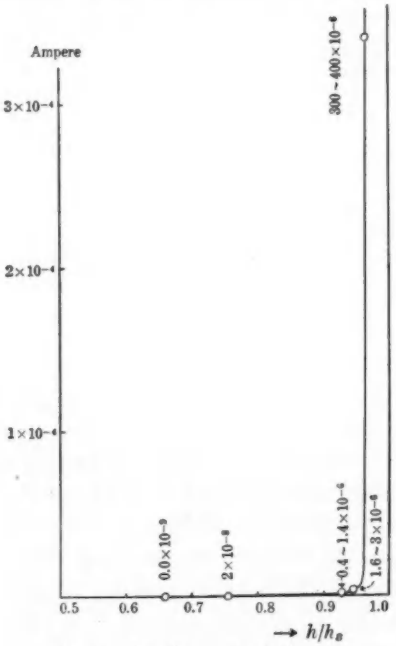


Fig. 3. The Current which flows through the Surface of KBr Crystal.

(4) This value may be more exact than that calculated from the real weight and calculated area of a small part of the sample.

(5) Durau, *Ann. Physik*, (4), **87** (1928), 307.

ductivity is measured passing the air of known humidity, when the circuit is closed only for a short time to avoid the polarization as far as possible.[6] (Fig. 3). In the dry air the conductance and consequently electrolysis are not observed at common temperature, while in the air of $h/h_s = 79.4/84$ alkali is detected at the cathode after a few hours.

Discussion of the Results. That potassium bromide or sugar is soluble in water means that it is more stable for ions or molecules at the crystal surface to exist hydrated by water molecules or in the dissolved state apart from the crystal. When water vapour is adsorbed at the surface of these crystals, it is easily supposed that this layer shows the affinity as the solvent to the ions (or molecules) at the surface though the properties of the adsorbed water under the influence of the surface field are somewhat different from those of the ordinary water.

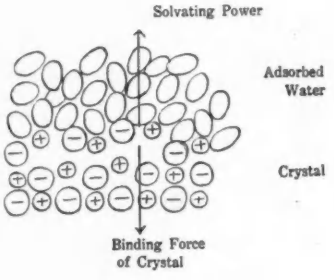


Fig. 4.

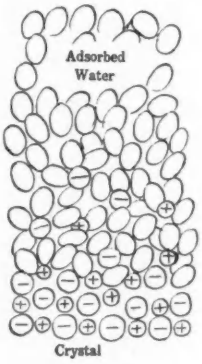


Fig. 5.

When the adsorbed quantity is little, complete hydration of ions (or molecules) is impossible as shown in Fig. 4 and so ions can not be separated from the crystal (accordingly no conductance in the case of electrolytes) though the binding force of the crystal may be weakened. When the adsorbed layer is thicker, comparatively perfect hydration being possible, some of ions (or molecules) can be dissolved in this (Fig. 5), and consequently conductance or electrolysis is observed in the case of electrolytes. As the ions are negatively adsorbed at the surface of the aqueous solution, it may be also true in the adsorbed layer

(6) Values of the same order were obtained when the sample shown in (b) was used

and so surface conductance is not observed until the layer has a certain thickness. This "solution" has the vapour tension lower than that of the usual saturated solution by the influence of the surface field of the crystal. This field may be more far-reaching than in the case of insoluble adsorbent as the surface of the solute is disturbed and becomes mobile when the solvent is adsorbed.

When the humidity of the atmosphere h becomes h_s, the adsorbed layer is thick enough and so the surface of which is not influenced by the crystal field and has the same vapour tension with that of the usual saturated solution. This vapour tension being independent of the thickness, the layer can become infinitely thick and deliquescence takes place. Accordingly adsorption of the solvent vapour and dissolution are continuous processes in the case of the soluble adsorbent.

The range of mobility of the surface ions (or molecules) is broadened by such an adsorption and rearrangement of the crystal surface takes place through this adsorbed layer so that the surface energy or area of the crystals may be decreased, and this results in the lumping of the powder. (Fig. 6. a→b).

Therefore lumping by humidity is not remarkable when the solubility is not large (sodium bicarbonate, potassium chlorate etc.) and is not observed in the case of insoluble substances (calcium phosphate, calcium carbonate etc.). The analogous phenomena can be observed for other solvent. For instance, sulphur particles which are large enough not to lump by sublimation lump in carbon disulphide vapour of which tension is lower than that of the saturated solution. A sample of sodium chloride sealed in a glass tube with water vapour lumped at 29° but not at 36°. This is easily explained as the result of the decrease of adsorption with rising temperature.

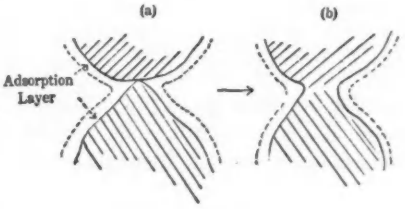


Fig. 6.

Humidity and Reaction between Solids. As the reaction between solid substances takes place at the contact point at the temperature where sublimation is negligible, the reaction velocity is increased when the surface ions (or molecules) become mobile and so the contact area is increased by the adsorption of the solvent vapour as shown above. Reactions which occur only in the solution may be also accelerated in this layer. (Fig. 7 and 6 a.) For examples, at common temperature tartaric

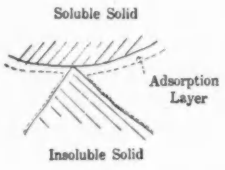


Fig. 7.

acid ($h_s = 86\%$) does not react with calcium carbonate in the desiccator but evolves carbon dioxide in the air of $h = 76\%$. The fact that this mixture lumps when the chemical change occurs shows that these phenomena have a common cause, mobility of tartaric acid molecule at the surface. On mixing calcium hydroxide and ammonium sulphate ($h_s = 81.2\%$) no change is observed in the air of $h = 63.0\%$, but when $h = 76.0\%$ ammonia smells strongly after a few hours, while the mixture of calcium hydroxide and magnesium ammonium phosphate, the latter being insoluble in water and so the surface mobility not increased by adsorption, does not evolve ammonia even when $h = 100\%$. The reaction between sodium chloride and sodium bisulphate is also greatly accelerated by the trace of water.[7] Balarev[8] studied many solid reactions at high temperature and found that a small quantity of water depresses the reaction temperature greatly and he attributed this to the relaxing of the binding of the surface molecules due to the adsorption, but he did not noticed the relation between this and the solubility. Though at high temperature adsorbed quantity is very little, the accelerating power is reported to be strong and may perhaps be catalytic, while at common temperature water seems to act as solvent.

Soluble and Insoluble Adsorbent. In the case of insoluble adsorbent which has been studied exclusively, the range of the surface force is very limited, and so monomolecular layer is formed when the adsorption takes place at low pressure. Though the multimolecular layer is formed when the pressure is higher, adsorbed molecules except in the first layer is held by the cohesion force among them. In the case of soluble adsorbent the range of force is broadened by the mobility of the surface ions (or molecules) due to the adsorption of solvent vapour, and this force, with the cohesion force among the adsorbed molecules, takes part in the formation of the multimolecular layer.

The authors express their thanks to Mr. S. Arakawa, Mr. H. Wakesima, and Mr. K. Yamazi for the kind helps.

Summary.

1) When some quantity of the solvent vapour is adsorbed by the solute crystal, a sort of solution is formed in the adsorbed layer.

(7) Isikawa, Masuda and Takai, *Bull. Inst. Phys. Chem. Research* (Tokyo), **14** (1935), 833.
(8) Balarev, many papers in *Z. anorg. Chem.*, (1924–1925).

2) Lumping of the powder, surface conductivity of the crystal, and the increase of the velocity of reactions between solids are explained as the result of the mobility of ions (or molecules) in this layer at the crystal surface.

Taihoku Higher School.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. II. On the Reduction and Bromination of Shonanic Acid.

By Nobutoshi ICHIKAWA.

(Received September 16th, 1936.)

In a previous communication[1] the author has reported the presence of a new acid (shonanic acid) among the volatile acidic ingredients of the wood of *Libocedrus formosana*, Florin, or "Shônan-Boku" and the general properties of the acid. The present communication deals with its reduction, the addition of bromine and some derivatives derived from the bromination product.

The behaviour of shonanic acid toward reducing agents is rather delicate and complicated. If shonanic acid be reduced with sodium and ethyl alcohol the product consists of about 92% of dihydroshonanic acid $C_{10}H_{16}O_2$ Γ_1 and 8% of tetrahydroshonanic acid $C_{10}H_{18}O_2$ (saturated acid), while if amyl alcohol be used instead of ethyl alcohol, about 75% dihydroshonanic and 25% tetrahydroshonanic acids resulted. In the latter case by using 20 times the theoretical amount of sodium necessary for the production of dihydro-acid, nearly all of the acid was converted into the tetrahydro-acid. With sodium amalgam dihydroshonanic acid can not be reduced any further, and with sodium and ethyl alcohol a very small portion of the acid is reduced to the tetrahydroshonanic acid, while in case of using excess of metallic sodium and amyl alcohol the reduction proceeds steadily until nearly all of the acid (dihydro-acid) is converted into the tetrahydro-acid.

(1) This Bulletin, **11** (1936), 759.

The reason why shonanic acid, which contains two conjugated double bonds, produces the saturated acid when reduced with amyl alcohol and large amount of sodium, may be explained as follows:—

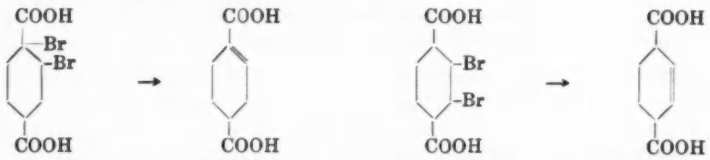
The reduction product of the first step, namely dihydroshonanic acid, may be isomerized to readily reducible α,β-unsaturated acid as in the case of $\Delta^{2,5}$-dihydroterephthalic[2] or of $\Delta^{1,3}$-dihydroterephthalic[3] acids by the action of amyl alcoholate at tolerable high temperature and the isomerized acids thus formed will be transformed into the saturated acid by further action of sodium and amyl alcohol.

On adding bromine to a solution of shonanic acid in ether, glacial acetic acid or carbon tetrachloride, two atoms of bromine will be taken up by the acid. The product, namely shonanic acid dibromide $C_{10}H_{14}O_2Br_2$, is a viscous liquid with a pale yellowish tint. It is unstable against permanganate solution even in cold but does not admit any further addition of bromine. Shonanic acid dibromide is soluble in alkaline solution and when treated with zinc dust in hot glacial acetic acid shonanic acid is regenerated with expulsion of bromine. From this fact it should be anticipated that the addition of two bromine atoms takes place at 1,2 or 3,4-position of the conjugated system. There are three modes of addition of bromine atom to the conjugated system as shown in the following:—

$$\text{R-CH=CH-CH=CH-R}' \xrightarrow{+2\text{Br}} \begin{cases} \text{R-CHBr-CHBr-CH=CH-R}' & \text{(A)} \\ \text{R-CH=CH-CHBr-CHBr-R}' & \text{(B)} \\ \text{R-CHBr-CH=CH-CHBr-R}' & \text{(C)} \end{cases}$$

In the case of (A) or (B) bromine atoms are taken away by zinc as to produce double bond, while in the case of (C) bromine atoms are substituted by hydrogen atoms. The examples of these reactions are shown in the following scheme:—

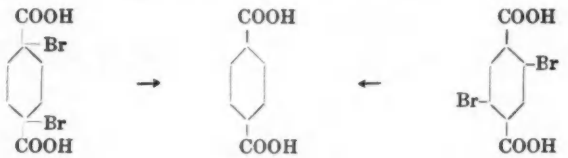
Example of the case of (A) or (B).[4]



Δ^1-Tetrahydroterephthalic acid dibromide — Δ^1-Tetrahydroterephthalic acid — Δ^2-Tetrahydroterephthalic acid dibromide — Δ^2-Tetrahydroterephthalic acid

(2) Baeyer, *Ann.*, **251** (1889), 281, 290, 306.
(3) Baeyer, *Ann.*, **269** (1892), 189.
(4) Baeyer, *Ann.*, **245** (1889), 169; Baeyer and Herb, *Ann.*, **258** (1890), 33.

Example of the case of (C).[5]



1,4-Dibromo-hexahydro-terephthalic acid — Hexahydro-terephthalic acid — 2,5-Dibromo-hexahydro-terephthalic acid

Following these examples, the addition of bromine to shonanic acid should represent the case of (A) or (B), and in the literature we find examples of this mode of addition in cases of sorbic acid[6] and cynnamylidene acetic acid.[7]

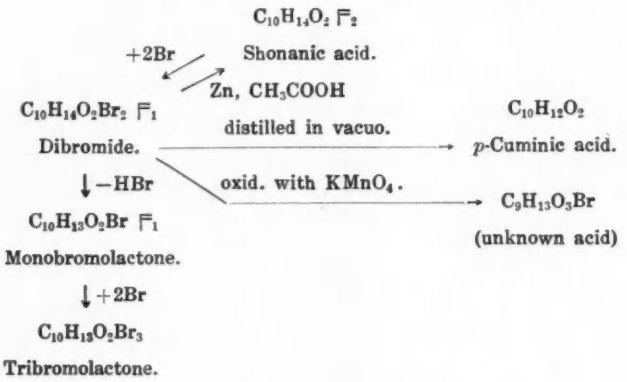
When shonanic acid dibromide is distilled in vacuo it decomposes to give *p*-cuminic acid. This formation of *p*-cuminic acid, however, must not be taken as the proof of the presence of isopropyl group in the molecule of shonanic acid, as shonanic acid as well as dihydroshonanyl alcohol on oxidation with permanganate give dimethylmalonic or dimethylglutaric acids, and no derivatives containing isopropyl group were obtained, the detailed description of which will be reported in the next communication.

Shonanic acid dibromide, on the other hand, on standing at ordinary temperature gradually turns into monobromolactone $C_{10}H_{13}O_2Br$ by giving off one mol of HBr. The substance is no more soluble in alkali but absorbs two more bromine atoms to give rise to a crystalline tribromolactone $C_{10}H_{13}O_2Br_3$, melting at 212° (with decomp.). The monobromolactone seems to be a γ-lactone from its mode of formation as analogous in cases of diallylmalonic,[8] phenylallylacetic,[9] or aticonic acids:[10] these substances add bromine to give dibromides and then giving off HBr gas form γ-lactones. A large number of experiments about the formation of lactones from Δ^{β}-, Δ^{γ}- and Δ^{α}-acids in which addition of bromine accompanied by fission of one mol of HBr are reported by J. Bougault,[11] by whom it was ascertained that Δ^{β}- and Δ^{γ}-acids give γ-lactones in these cases.

(5) Baeyer, *Ann.*, **245** (1889), 176, 151.
(6) Auwers and Heyna, *Ann.*, **434** (1923), 140.
(7) Auwers and Müller, *Ann.*, **434** (1923), 165.
(8) Hjelt, *Ann.*, **216** (1882), 61.
(9) Wislicenus and Goldstein, *Ber.*, **29** (1896), 2601.
(10) Fittig, *Ann.*, **304** (1899), 133.
(11) Bougault, *Compt. rend.*, **139** (1904), 864; **143** (1906), 398; **146** (1906), 140.

On oxidation with alkaline permanganate shonanic acid dibromide gives a crystalline bromo-acid $C_9H_{13}O_3Br$ (m.p. 239° with decomp.), the nature of which is not yet clear.

The following scheme shows the various changes mentioned above:



Experimental.

I. Action of reducing agents on shonanic acid. (1) *Action of sodium amalgam.* 10 g. of shonanic acid was dissolved in sodium bicarbonate solution and 300 g. of sodium amalgam (2.5%) was added with constant stirring and cooling while CO_2 gas was introduced into the reaction mixture in order to neutralize NaOH set free during the course of the reaction. After all the sodium amalgam has been consumed, the alkaline solution was acidified with dilute sulphuric acid when an organic acid made appearance which was collected with ether. After removal of the solvent the residue was fractionally distilled under diminished pressure and it was found that almost whole of the substance distilled at 134–135° under 6 mm. The distillate solidified to a compact mass on standing in cold, which melted at 40° after one recrystallization from light petroleum ether. The amide prepared therefrom melted at 116–117° and showed no depression of the melting point when mixed with shonanic amide. (Analysis of the silver salt: Ag, 39.55. Calculated for $C_{10}H_{13}O_2Ag$: Ag, 39.53%.)

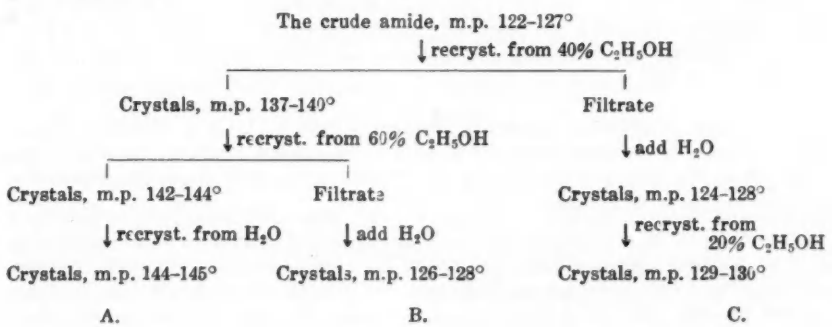
Thus it was shown that the reduction of shonanic acid can not be achieved by sodium amalgam as in the case of dihydro-*p*-xylic acid. The author, therefore, made a trial to obtain dihydro-acid $C_{10}H_{16}O_2$ F_1 from shonanic acid by means of sodium and amyl alcohol, as by this treatment the above-mentioned dihydro-*p*-xylic acid gives tetrahydro-*p*-xylic acid.

(2) *Reduction with sodium and amyl alcohol.* 5 g. of shonanic acid was dissolved in 100 c.c. of amyl alcohol and 3.5 g. of metallic sodium (2.5 times of the theoretical amount necessary to produce $C_{10}H_{16}O_2$ F_1 from $C_{10}H_{14}O_2$ F_2) was added in small portions, heating the mixture, and adding water (about 2–3 c.c. at a time)

from time to time in order to ensure the complete dissolution of the metallic sodium. After all the sodium has been taken up, the reaction product was poured into water and the aqueous layer separated and shaken thoroughly with ether to remove traces of amyl alcohol. The alkaline solution was then acidified with dilute sulphuric acid and the organic acid set free was extracted with ether. The extract, after evaporating the excess of the solvent, was rectified under reduced pressure. B.p. 146–147°/9 mm.; d_4^{20} 1.0217; n_D^{20} 1.4892; M.R. obs. 47.48, calculated for $C_{10}H_{16}O_2$ F_1 47.35; bromine value 711 (0.1365 g. absorbed 0.097 g. of bromine), calculated for $C_{10}H_{16}O_2$ F_1 952.

The difference between the theoretical and the experimental bromine values may be attributed to the presence of the saturated acid (tetrahydroshonanic acid, $C_{10}H_{18}O_2$) and this conjecture was proved correct by the fact that tetrahydroshonanic amide was actually obtained from the reduction product. The ratio of saturated and unsaturated acid can roughly be calculated from the theoretical and experimental bromine values as follows: saturated acid 74.6, unsaturated acid 25.4%. (Found: C, 71.04, 70.96; H, 10.13, 10.06. Calculated for $C_{10}H_{16}O_2$: C, 71.4; H, 9.5; $C_{10}H_{18}O_2$: C, 70.6; H, 10.6%. Analysis of the silver salt: Ag, 39.27. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.24; $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Amide. The acid chloride was prepared from the acid (1 g.) and phosphorus trichloride as usual and it was added to cold aqueous ammonia to obtain the amide. The amide melted at 122–127°, which was subjected to fractional recrystallization as shown below:



Crystals A were proved to be identical with tetrahydroshonanic amide prepared from saturated acid (tetrahydro-acid) obtained by catalytic reduction of shonanic acid; crystals B might have been crude mixture of A and C, but on account of the scarcity of the substance further purification was not carried out; crystals C represented dihydroshonanic amide whose melting point remained constant on further purifications. (Found: N, 8.56. Calculated for $C_{10}H_{17}ON$: N, 8.4%.) Other evidences for the presence of the saturated acid therein may also be recognized among the experimental data observed in the analysis of the silver salt, elementary analysis and bromine value.

(3) *Reduction with a large amount of sodium and amyl alcohol.* 10 g. of the acid dissolved in 300 c.c. of amyl alcohol was kept hot on a boiling water-bath and 30 g. of sodium was added in small portions with vigorous stirring. 2–5 c.c. of water was added several times during the course of the reaction in order to promote the reaction. The reaction product was poured into water, stirred vigorously for 10 minutes and the alkaline layer was separated. The alkaline solution was acidified and the organic acid set free was extracted with ether. The extract after removal of the solvent was subjected to fractional distillation under reduced pressure. At the beginning of the distillation isovaleric acid, produced as by-product,[12] distilled and then the main fraction boiling at 143–144°/9 mm. came over. The distillate was rectified once more and thus an acid with the following properties was obtained: b.p. 140–141°/8 mm.; d_4^{20} 0.9863; n_D^{20} 1.4665; M.R. obs. 47.78, calculated for $C_{10}H_{18}O_2$ 47.72; acid value 336.4 (0.5238 g. required 32.11 c.c. of 0.098 N NaOH), calculated for $C_{10}H_{18}O_2$ 329.4; bromine value nil. (Found: C, 70.44, 70.42; H, 10.61, 10.60. Calculated for $C_{10}H_{18}O_2$: C, 70.58; H, 10.58%. Analysis of the silver salt: Ag, 38.90. Calculated for $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Contrary to the previous case the product was an entirely saturated acid (tetrahydroshonanic acid) the amide showing the same melting point as tetrahydroshonanic amide.

Acid chloride. The acid chloride was prepared in the usual manner from 3 g. each of the acid and phosphorus trichloride. Its properties were as follows: b.p. 115–116°/20 mm.; d_4^{30} 1.016; n_D^{20} 1.4713.

Amide. The amide was obtained by the interaction of the acid chloride and aqueous ammonia in plate crystals with pearly lustre, which melted at 143–144° after a crystallization from 50% ethyl alcohol. (Found: N, 8.23. Calculated for $C_{10}H_{19}ON$: N, 8.28%.)

—**II. Action of reducing agents on dihydroshonanic acid.** (1) *Catalytic hydrogenation of dihydroshonanic acid.* As already stated in the previous communication, it was found that dihydroshonanic acid absorbs two atoms of hydrogen to give tetrahydroshonanic acid $C_{10}H_{18}O_2$.

(2) *Action of sodium amalgam.* 5 g. of dihydroshonanic acid (containing ca. 92% of dihydroshonanic acid obtained by the experiment IV-(6) in the previous communication) was dissolved in an excess of 10% sodium hydroxide solution and was treated with 400 g. of sodium amalgam (2.5%) (6 times the calculated amount to give $C_{10}H_{18}O_2$) at ordinary temperature with vigorous stirring. The product showed the following properties: b.p. 143–144°/7 mm.; d_4^{30} 1.0328; n_D^{30} 1.4987; M.R. obs. 47.74, calculated for $C_{10}H_{16}O_2$ F_1 47.35; bromine value 885 (0.1922 g. absorbed 0.1698 g. of bromine), calculated for $C_{10}H_{16}O_2$ F_1 952.

That the unsaturated acid remains practically unchanged is clear from the bromine value, which tells that dihydroshonanic acid is not at all affected by sodium amalgam.

Amide. The amide was prepared from the acid chloride and aqueous ammonia which melted at 129–130° and was proved to be identical with dihydroshonanic amide

(12) Dumas and Stas, *Ann.*, **35** (1840), 143.

by melting in admixture with that obtained in the experiment IV-(6) (previous communication[1]).

(3) *Reduction with sodium and ethyl alcohol.* 3 g. of dihydroshonanic acid was dissolved in 100 c.c. of ethyl alcohol and 3.5 g. of sodium (3 times of the theoretical amount of sodium necessary to produce $C_{10}H_{15}O_2$ from $C_{10}H_{19}O_2F_1$) was added in small portions. The product showed the following properties: b.p. 141–143°/7 mm.; d_4^{30} 1.0298; n_D^{30} 1.4966; M.R. obs. 47.71, calculated for $C_{10}H_{19}O_2F_1$ 47.35; bromine value 875 (0.1108 g. absorbed 0.0906 g. of bromine), calculated for $C_{10}H_{19}O_2F_1$ 952.

The amount of the saturated acid calculated from the bromine value is ca. 15% showing an increase of the saturated acid by 7% as compared with the starting substance.

Amide. The amide prepared as usual from the acid chloride and aqueous ammonia melted at 107–120° without any purification, which was then subjected to fractional recrystallization as follows:—

The crude amide, m.p. 107–120°
↓ recryst. from 40% C_2H_5OH

Crystals, m.p. 123–133°
↓ recryst. from 60% C_2H_5OH

Crystals, m.p. 140–144°
↓ recryst. from 60% C_2H_5OH
Crystals, m.p. 142–145°
A.

Crystals from the filtrate, m.p. 124–127°
↓ recryst. from 20% C_2H_5OH
Crystals, m.p. 127–129°
↓ recryst. from H_2O
Crystals, m.p. 129°
B.

Crystals from the filtrate, m.p. 118–124°
↓ recryst. from 20% C_2H_5OH
Crystals, m p. 126–129°
↓ recryst. from H_2O
Crystals, m.p. 128–129°
C.

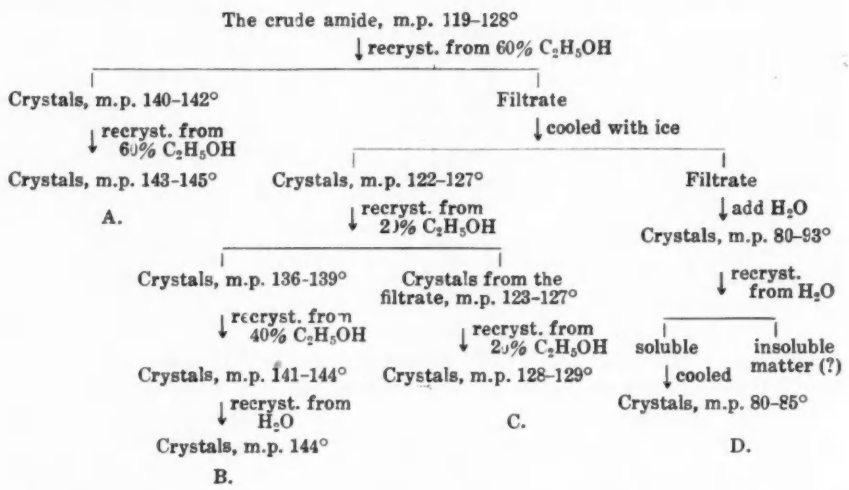
Owing to the scarcity of the material crystals A were without further purification mixed with tetrahydroshonanic amide and the melting point examined. They melted at 142–144°, from which it is obvious that this substance is tetrahydroshonanic amide. Crystals B and C were identified as dihydroshonanic amide in like manner.

(4) *Reduction with sodium and amyl alcohol.* 3 g. of dihydroshonanic acid (preparation of the experiment IV-(6) of the previous report, containing 92% dihydroacid) was dissolved in 100 c.c. of amyl alcohol and was reduced with 3.5 g. of sodium. The product had the following properties: b.p. 142–144°/7 mm.; d_4^{30} 1.0160; n_D^{30} 1.4870; bromine value 378 (0.1635 g. absorbed 0.0616 g. of bromine), calculated for $C_{10}H_{19}O_2F_1$ 952.

The approximate amount of the saturated acid in the reaction product is about 60% as calculated from the bromine value. (Analysis of the silver salt: Ag, 39.03. Calculated for $C_{10}H_{15}O_2Ag$: Ag, 39.24; $C_{10}H_{17}O_2Ag$: Ag, 38.96%.)

Amide. The acid chloride obtained from 1.3 g. of the acid and 1.5 g. of phosphorus trichloride was treated with aqueous ammonia, and the crude amide

thus obtained melted at 119–128° without any purification, which was fractionally recrystallized as follows.



The crystals A and B were found to be identical with tetrahydroshonanic amide by observing the melting point of mixtures, while the crystals C were found to be identical with dihydroshonanic amide. The crystals D were not further purified as the quantity available became scarce but it can not be considered as crude crystals of C as the former is readily soluble in water while the latter is not.

(5) *Reduction with a large amount of sodium and amyl alcohol.* 3 g. of dihydroshonanic acid was dissolved in 100 c.c. of amyl alcohol and was treated with 10 g. of sodium as usual. The product showed the following properties: b.p. 141–143°/7 mm.; d_4^{30} 0.9930; n_D^{30} 1.4703; M.R. obs. 47.74, calculated for $C_{10}H_{18}O_2$ 47.72; bromine value 26 (0.1472 g. absorbed 0.0038 g. of bromine).

The percentage of the saturated acid therein was found to be about 97%.

Amide. The amide was prepared from the acid chloride (prepared from 2 g. of the acid and 3 g. of phosphorus trichloride) and aqueous ammonia. It melted at 144° after one recrystallization from 60% ethyl alcohol and was found to be identical with tetrahydroshonanic amide obtained by catalytic hydrogenation of shonanic acid.

III. Some derivatives of shonanic acid containing bromine. (1) *Shonanic acid dibromide.* To a well-cooled solution of shonanic acid (acid 10 g. in ether 100 c.c.) 10 g. of bromine was added drop by drop with constant shaking. The colour of the ethereal solution acquired yellowish tint and on removal of the solvent under diminished pressure there remained a colourless viscous oily substance, which showed no tendency of solidification even kept at −5° for several days. The dibromide thus obtained does not admit further addition of bromine whereas it is easily acted on by dilute permanganate solution at 0°. On standing at the ordinary temperature

a portion of the dibromide was gradually converted into grayish monobromolactone (see below).

The dibromide could not be distilled without decomposition and the physical properties of the crude preparation were as follows: d_4^{30} 1.603; n_D^{30} 1.5330; M.R. obs. 63.10, calculated for $C_{10}H_{14}O_2Br_2$ 62.78. (Found: C, 37.27; H, 4.35; Br, 48.78. Calculated for $C_{10}H_{14}O_2Br_2$: C, 36.81; H, 4.29; Br, 49.06%.)

(2) *Regeneration of shonanic acid from its dibromide.* 10 g. of shonanic acid dibromide freshly prepared as above was dissolved in 60 c.c. of glacial acetic acid, kept cool with the freezing mixture and 50 g. of zinc dust was added in small portions. After all zink dust has been added the reaction mixture was then warmed on a boiling water-bath for an hour. It was then poured into water and the oily acidic substance separated was extracted with ether. The ethereal solution was washed with water to remove acetic acid present, dried over anhydrous sodium sulphate and the ether was distilled off. The reddish brown substance remaining behind was fractionally distilled under reduced pressure, when 3.8 g. of acidic substance came over at 140°/7 mm. It contained no bromine at all, as it gave no Beilstein's flame reaction. The amide prepared from the acid chloride (b.p. 98°/12 mm.) of the substance and aqueous ammonia melted at 116–117° after recrystallization from 50% ethyl alcohol, it was identical with shonanic amide. Thus, by the action of zinc and glacial acetic acid, shonanic acid was regenerated from its dibromide.

(3) *The formation of monobromolactone from the dibromide.* 6.5 g. of shonanic acid dibromide was placed in a round flask and warmed on the water-bath at 40–50° for 4 hours under 40–50 mm. It was then dissolved in ether and by shaking with dilute sodium carbonate solution the unchanged acid was removed. From the ethereal solution a substance with the following properties was obtained (Yield 2.4 g.): d_4^{30} 1.4540; n_D^{20} 1.544; M.R. obs. 53.21, calculated for $C_{10}H_{15}O_2Br$ 52.81.

The substance is insoluble in alkaline solution, unstable against permanganate and absorbs bromine in cold, showing the substance to be unsaturated. The substance could not be distilled without decomposition. Bromine value 644.6 (0.7983 g. absorbed 0.5146 g. of bromine), calculated for $C_{10}H_{13}O_2Br$ 653.1. (Found: Br, 32.68. Calculated for $C_{10}H_{13}O_2Br$: Br, 32.65%.)

(4) *Preparation of tribromolactone from monobromolactone.* To a solution of 5 g. of monobromolactone in 50 c.c. of glacial acetic acid 5 g. of bromine was added in the cold, which was readily absorbed and a crystalline substance deposited on standing. The solution was kept cool over night and the crystalline substance was filtered, washed with cold glacial acetic acid then with ether. Yield 8.3 g. (91% of the theoretical). The tribromolactone, thus prepared, melted at 209° (with decomposition), insoluble in alkali, ether, ethyl alcohol, chloroform and glacial acetic acid and sparingly soluble in boiling alcohol, benzene and petroleum ether. When recrystallized from boiling alcohol the melting point was elevated to 212° (with decomposition). (Found: C, 29.34; H, 3.25; Br, 58.74. Calculated for $C_{10}H_{13}O_2Br_3$: C, 29.65; H, 3.21; Br, 59.23%.)

(5) *The formation of* p-*cuminic acid from shonanic acid dibromide.* When shonanic acid dibromide (10 g.) was subjected to distillation under reduced pressure

the evolution of hydrogen bromide set in at first and there happened no remarkable change until the temperature of the oil bath attained 200°, when suddenly a vigorous evolution of gas took place and on further heating a fraction boiling at 146°/7 mm. distilled over. This fraction on standing deposited a crystalline substance which was spread over a porous plate to remove liquid substance and then it was recrystallized from 40% ethyl alcohol. It melted at 119–120°. Another crop of crystals was obtained from the filtrate by the addition of water, which also melted at 119° after one recrystallization from 40% ethyl alcohol. The substance bears an acidic characteristic and is inert against permanganate and does not give flame colour reaction of Beilstein, showing the absence of bromine. Acid value 341.2 (0.1716 g. required 10.52 c.c. of 0.102N NaOH), calculated for $C_{10}H_{12}O_2$ 341.5. (Found: C, 73.35; H, 7.57. Calculated for $C_{10}H_{12}O_2$: C, 73.17; H, 7.31%. Analysis of the silver salt: Ag, 39.78. Calculated for $C_{10}H_{11}O_2Ag$: Ag, 39.82%.)

Acid chloride. A mixture of 1.4 g. of the acid and 1.5 g. of phosphorus pentachloride was heated on the water-bath for 20 minutes. The product distilled at 107–109°/15 mm. Yield 0.8 c.c.

Amide. The amide was prepared as usual by the interaction of the acid chloride and aqueous ammonia. It melted at 152–153° when recrystallized from 60% ethyl alcohol.

Among the acids of the formula $C_{10}H_{12}O_2$, *p*-cuminic acid melts at 119–120° and its amide at 152–153°. In order to ascertain that the acid under investigation is identical with *p*-cuminic acid the latter was prepared from *p*-cuminol by kali-fusion.

To molten potassium hydroxide (7 g.) in a nickel crucible, 5 g. of *p*-cuminol was added drop by drop with constant agitation. The reaction product was then treated with water and *p*-cuminic acid produced was liberated in the usual way and recrystallized from alcohol. It melted at 119° and on mixing it with the acid under investigation showed no depression of the melting point. Thus it is evident that the acid obtained by the decomposition of shonanic acid dibromide is *p*-cuminic acid.

IV. Oxidation of shonanic acid dibromide with potassium permanganate. To a well-cooled solution of shonanic acid dibromide (10 g.) in 5% sodium carbonate solution (300 c.c.) dilute permanganate solution ($KMnO_4$ 26 g. in 600 c.c. H_2O) was added drop by drop with constant stirring. The reaction mixture was left over night in an atmosphere of carbon dioxide, filtered from manganese dioxide and the alkaline solution thus obtained was evaporated nearly to dryness on the water-bath. The organic acid liberated by acidification with dilute sulphuric acid was extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate and then the solvent was distilled away. The remainder crystallized on cooling in prismatic needles which was purified by washing with chloroform and twofold recrystallizations from absolute alcohol. It melted at 239° (with decomposition). The substance is insoluble in cold alcohol, chloroform, benzene and petroleum ether and soluble in alkali from which the original acid can be regenerated by the addition of mineral acid. The presence of bromine atom in the molecule of the acid was recognized by Beilstein's flame colour reaction. (Found: C, 43.37; H, 5.10; Br, 32.12. Calculated

for $C_5H_{10}O_3Br_2$: C, 43.37; H, 5.22; Br, 31.92%. Analysis of the silver salt: Ag, 30.41. Calculated for $C_5H_{11}O_3BrAg$: Ag, 30.33%.)

The acid being monobasic the third atom of oxygen therein may exist either as a carbonyl or as a hydroxyl oxygen, but as the material was scanty, it was not studied any further.

In conclusion, the author wishes to express his sincere thanks to Prof. Kinzô Kafuku for his kind guidance.

Department of Industry,
Government Research Institute of Taiwan.

Studies on the Constitution of Shonanic Acid, One of the Two Characteristic Volatile Acids from the Wood of *Libocedrus formosana*, Florin. III. Studies on the Oxidation of Shonanic Acid.

By Nobutoshi ICHIKAWA.

(Received September 16th, 1936.)

Shonanic acid, when oxidized in cold with dilute potassium permanganate solution, gives a crystalline dibasic acid of the formula $C_5H_8O_4$. The acid purified by sublimation in vacuo melts at 184–186° (with decomp.), its amide melting at 259–260°. There are four possible constitutional formulæ for this acid, viz.,

(1) $HOOC\text{-}(CH_2)_3\text{-}COOH$ Pyrotartaric acid, m.p. 97°.

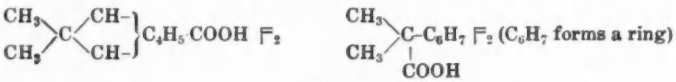
(2) $CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}COOH$ Methylsuccinic acid, m.p. 115°, 102°, 112.5°.

(3) $CH_3\text{-}CH_2\text{-}CH(COOH)_2$ Ethylmalonic acid, m.p. 111.5°.

(4) $(CH_3)_2C(COOH)_2$ Dimethylmalonic acid, m.p. 186° (with decomp.).

As the present acid $C_5H_8O_4$, on heating somewhat above its melting point, loses exactly one mol of carbon dioxide and transforms into isobutyric acid, it is obvious that the acid has two carboxyl groups in union with one carbon atom, i.e. it must be dimethylmalonic acid. The formation of dimethylmalonic acid indicates that shonanic acid should be repre-

sented by I or II. In case of I the two carboxyl groups (in dimethylmalonic acid) were newly formed as the result of oxidation, while in the latter case one of the carboxyl groups is the originally contained one.



I. II.

In order to determine the structural feature of the ring-forming nucleus of shonanic acid, the following methods were adopted.

(1) Preparation of hydrocarbon with the same number of carbon atoms as shonanic acid by reducing carboxyl group to methyl group. The resulting hydrocarbon was compared with the known hydrocarbons of the same formula in regard to their physical properties.

(2) Preparation of hydrocarbon with nine carbon atoms by eliminating the carboxyl group on heating the acid with soda-lime.

(3) Conversion of shonanic acid into known substances by oxidizing the side chain or substituents in the nucleus of shonanic acid.

The results of the experiments were as follows.

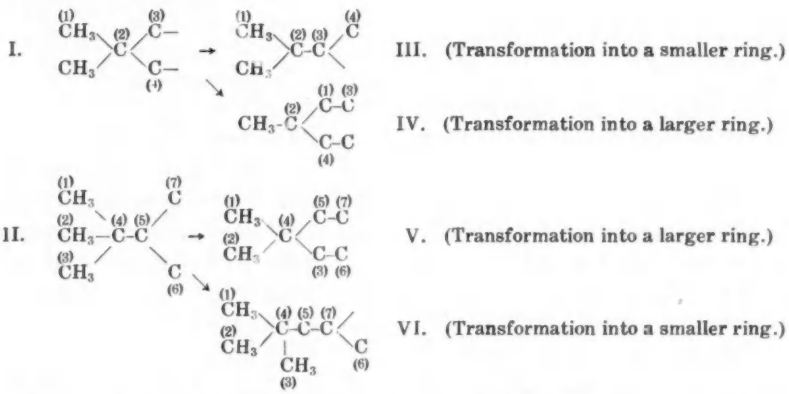
(1) The hydrocarbon prepared by heating shonanic acid and tetrahydroshonanic acid respectively with hydroiodic acid in a sealed tube showed the following properties:

Hydrocarbon from shonanic acid.	Hydrocarbon from tetrahydroshonanic acid.
b.p. 157–158.3°/754 mm.	b.p. 158.5°/765 mm.
d_4^{20} 0.7866	d_4^{20} 0.7872
n_D^{20} 1.4344	n_D^{20} 1.4338

Whether the starting substance be the unsaturated shonanic acid or the saturated tetrahydroshonanic acid, that the product formed by the action of hydroiodic acid should represent the same hydrocarbon is experimentally assured as far as the physical properties are concerned. This hydrocarbon, as should be expected from the known partial structure of the original acid, contains an arrangement I or II, provided that no inversion takes place throughout the reduction by hydroiodic acid.

Thus in comparing it with known hydrocarbon, such ones containing a dimethyl or trimethyl group should be adopted, and further more, taking

into consideration the ring transformation often effected by hydroiodic acid, the cases of III to VI, viz.:


I.
III. (Transformation into a smaller ring.)
IV. (Transformation into a larger ring.)
II.
V. (Transformation into a larger ring.)
VI. (Transformation into a smaller ring.)

The properties of hydrocarbons $C_{10}H_{20}$ with atom groups mentioned above were tabulated in Table 1. As seen from the table the hydrocarbons $C_{10}H_{20}$ have the general value 0.78–0.81 for the density, 1.43–1.45 for the refractive index. Those with six-membered ring have the boiling points 166–171°, while those with five-membered ring have values lower than 160°. On comparing the physical properties of the hydrocarbon from shonanic acid with those of the known hydrocarbons it is likely that the former possesses a five-membered ring, but this should not at once extended to shonanic acid itself, as the ring transformation might have ensued by the action of hydroiodic acid as in the transformations of benzene to methylcyclopentane and cyclohexyl iodide or cyclohexanol to methylcyclopentane. But judging from its physical properties, it is evident that the hydrocarbon obtained from shonanic acid is either a compound with a five- or six-membered ring system.

(2) With a view to obtain a hydrocarbon C_9H_{18} tetrahydroshonanic acid was heated with soda-lime, when, contrary to the expectation, an unsaturated hydrocarbon C_9H_{16}, which showed the following properties, was obtained. B.p. 145–148°; d_4^{29} 0.8128; n_D^{29} 1.4593.

The attempt to obtain its nitrosochloride or nitrosite in the crystalline state was futile. Next, in order to study the ring system of the hydrocarbon obtained, its physical properties were compared with those of known hydrocarbons of the same formula C_9H_{16}[=]$_1$. For this purpose the following hydrocarbons were chosen (Table 2), taking into consideration the ring transformation or migration of atom groups which might have been accomplished by heating with soda-lime.

Table 1.

Substance	d	n_D	B.p.
o-Menthane[1]	0.8135 $(^{21}_{0})$	1.447 (21)	171°
d-*m*-Menthane[2]	0.8116 $(^{25}_{0})$	1.446 (23)	167–168°
l-*m*-Menthane[3]	0.7938–0.7956 $(^{20}_{0})$	1.4358–1.4355 (20)	167–168°
i-*m*-Menthane[1]	0.7965 $(^{24}_{0})$	1.440 (24)	166–167°
p-Menthane[4]	0.7974 $(^{20}_{4})$	1.4380 (20)	172°
Hexahydrodurol[5]	0.811 $(^{20}_{4})$	1.4451 (20)	169–170.5°
1,3-Diethyl-cyclohexane[6]	0.7957 $(^{22}_{4})$	1.4388 (20)	169–171°
Butyl-cyclohexane[7]	0.8178 $(^{20}_{4})$	—	178–180°
tert-Butyl-cyclohexane[8]	0.8305 $(^{16}_{4})$	1.4556 (16)	166–167°
1-Methyl-3-propyl-cyclohexane[9]	0.7895 $(^{21}_{4})$	1.4352 (21)	169–170°
1,2-Dimethyl-3-isopropyl-cyclopentane[10]	0.786 $(^{16})$	1.4337 (16)	146–148°
Hydrocarbon from thujane[11]	0.7923 $(^{20}_{0})$	1.4377	157°
Hydrocarbon from shonanic acid	0.7872 $(^{19}_{4})$	1.4338 (19)	158.5°

Table 2.

Substance	d	n_D	B.p.
1-Propyl-cyclohene[12]	0.838 $(^{19})$	1.4579 (19)	154–156°
Propyliden-cyclohexane[13]	0.8210 $(^{19})$	1.4631 (19)	157–158°
Δ^1-Tetrahydrocumol[14]	0.8290 $(^{20})$	1.4606 (20)	155–157°
Isopropyliden-cyclohexane[15]	0.836 $(^{20})$	1.4723 (20)	160–161°

(1) Sabatier and Murat, *Compt. rend.*, **156** (1913), 186.
(2) Sabatier and Murat, *ibid.*, **156** (1913), 187.
(3) Kishner, *Chem. Zentr.*, **83** (1912), I, 1456.
(4) Smirnow, *Chem. Zentr.*, **81** (1910), I, 740.
(5) Willstätter and Hatt, *Ber.*, **45** (1912), 1473.
(6) Zelinsky and Rudewith, *Ber.*, **28** (1895), 1343.
(7) Douris, *Compt. rend.*, **157** (1913), 57.
(8) Halse, *J. prakt. Chem.*, [2], **92** (1915), 41.
(9) Beilstein, "Handbuch der organischen Chemie," 4. Aufl., Bd. 5, Erstes Ergänzungswerk, 20 (1931).
(10) Godchot and Taboury, *Compt. rend.*, **156** (1913), 472.
(11) Kishner, *Chem. Zentr.*, **83** (1912), I, 1457.
(12) Wallach, Churchill, and Rentschler, *Ann.*, **360** (1908), 58.
(13) Wallach, Churchill, and Rentschler, *Ann.*, **360** (1908), 56.
(14) Wallach and Mallison, *Ann.*, **360** (1908), 69.
(15) Wallach and Mallison, *Ann.*, **360** (1908), 68.

Table 2.—(*Concluded*)

Substance	d	n_D	B.p.
1-Methyl-2-ethyliden-cyclohexane[16]	0.823 (^{0})	1.47	158°
1-Methyl-3-ethyliden-cyclohexane[17]	0.813 (^{0})	1.4584	153°
1-Methyl-3-ethyl-cyclohexene-(2 or 3)[18]	0.8154 ($^{19}_{0}$)	1.4538 (19)	148–149°
1-Methyl-4-ethyl-cyclohexene-(3)[19]	0.8169 ($^{16}_{4}$)	1.453 (16)	149°
1-Methyl-4-ethyliden-cyclohexane[20]	0.810 (^{20})	1.4571 (20)	152–153°
1,1,2-Trimethyl-cyclohexene-(2)[21]	0.8217 (^{20})	1.456 (20)	146.2–147.2°
1,1,3-Trimethyl-cyclohexene-(2)[22]	0.803 (^{20})	1.446 (21.5)	139–142°
1,1,4-Trimethyl-cyclohexene-(3)[23]	0.8032 ($^{18.8}_{4}$)	1.4415 (23)	139–140°
1,2,3-Trimethyl-cyclohexene-(1)[24]	0.8347 ($^{11.7}_{4}$)	1.463 (11.7)	149–150°
1,2,4-Trimethyl-cyclohexene-(4)[25]	0.8078 ($^{16}_{4}$)	1.450 (16)	144–146°
1,3,5-Trimethyl-cyclohexene-(1)[26]	0.7965 (^{21})	1.4447 (21)	142.5–143.5°
3,5-Dimethyl-1-methylen-cyclohexane[27]	0.7922 ($^{14}_{4}$)	1.446 (14)	135–136°
1-Methyl-3-isopropyl-cyclopentene-(1)[28]	0.801 (^{20})	1.4478 (20)	144–146°
1-Methyl-3-isopropyl-cyclopentene-(2)[29]	0.791 (^{22})	1.4380 (22)	138–139°
Apofenchene[30]	0.794 (^{21})	1.4403 (22)	142–143°
1-Methyl-2-isopropyliden-cyclopentane[31]	0.8104 ($^{20}_{0}$)	1.4518	149–151°
1-Methyl-2-isopropenyl-cyclopentane[31]	0.8006 (^{20})	1.4455	141–143°
Pulegene[32]	0.791 (^{22})	1.4380	138–139°
1,1,2-Trimethyl-3-methylen-cyclopentane[33]	—	—	138–140°
1,1,2,5-Tetramethyl-cyclopentene-(3)[34]	0.8034 (^{20})	1.44406 (20)	133–135°
Hydrocarbon from tetrahydroshonanic acid	0.8129 ($^{19}_{4}$)	1.4595 (19)	145–148°

(16) Murat, *Ann. chim.*, [8], **16** (1909), 125.
(17) Wallach and Evans, *Ann.*, **360** (1908), 51.
(18) Zelinsky and Gutt, *Ber.*, **35** (1902), 2140; Zelinsky and Zelikow, *Ber.*, **34** (1901), 3255
(19) Sabatier and Mailhe, *Compt. rend.*, **142** (1906), 439.
(20) Wallach and Rentschler, *Ann.*, **365** (1909), 271.
(21) v. Auwers and Lange, *Ann.*, **409** (1915), 174.
(22) Tiemann, *Ber.*, **33** (1900), 3711.
(23) v. Auwers and Lange, *Ann.*, **409** (1915), 167.
(24) v. Auwers and Krollpfeiffer, *Ber.*, **48** (1915), 1231.
(25) v. Auwers, *Ann.*, **420** (1919), 105.
(26) v. Auwers, Hinterseber, and Treppmann, *Ann.*, **410** (1915), 270.
(27) v. Auwers, Hinterseber, and Treppmann, *Ann.*, **410** (1915), 272.
(28) Semmler, *Ber.*, **37** (1904), 237.
(29) Wallach, Collmann, and Thede, *Ann.*, **327** (1903), 131.
(30) Wallach, *Ann.*, **369** (1909), 83.
(31) Kishner, *Chem. Zentr.*, **83** (1912), II, 1925.
(32) Wallach, Collmann, and Thede, *Chem. Zentr.*, **73** (1902), I, 1925.
(33) Bouveault and Blanc, *Compt. rend.*, **136** (1903), 1461.
(34) Tiemann, *Ber.*, **30** (1897), 595.

As seen from Table 2, the hydrocarbons with six-membered ring system have values 0.80–0.83 for density while those with five-membered ring 0.79–0.81. Thus it can not be decided by comparing the densities whether the hydrocarbon under investigation is of five- or six-membered ring. Viewed from refractive indices, hydrocarbon of six-membered ring system have values 1.44–1.47 while those of five-membered ring system values 1.43–1.45. The actual hydrocarbon has $n_D^{20} = 1.4595$ and consequently is likely to be one with six-membered ring system, but it should not be strongly taken into account, as its boiling point is found to be 145–148° which is close to those of hydrocarbons with five-membered ring as well as with six-membered ring.

(3) The attempt to obtain some known derivatives from shonanic acid by oxidation at last succeeded by the use of dilute nitric acid as oxidant. When shonanic acid was heated with dilute nitric acid for some hours *o*-dinitrobenzene was obtained with a fairly good yield. Though it can not easily be elucidated under what mechanism the acid was converted into *o*-dinitrobenzene, the formation of it may be taken as an evidence for the presence of six-membered ring in shonanic acid molecule, unless other data appear which are rigorously against the above reasoning.

Experimental.

I. Oxidation of shonanic acid with potassium permanganate. 600 c.c. of 4% potassium permanganate solution was added drop by drop to a well-cooled solution of the acid (5 g. of the acid in 500 c.c. of 7% Na_2CO_3 solution) with vigorous stirring. After all the permanganate solution has been added the reaction mixture was warmed on the water-bath at 40–50° for 30 minutes and filtered while hot in order to remove manganese dioxide precipitated. The filtrate was then evaporated nearly to dryness, acidified with dilute sulphuric acid and extracted with ether. On distilling off the solvent there remained about 3.5 g. of reddish yellow sticky substance, which on standing at the ordinary temperature for 7–10 days nearly half of the contents solidified to a crystalline mass. The crystalline substance thus obtained was filtered and spread over a porous plate to remove liquid matter.

(1) *The crystalline portion.* The crystalline substance thus separated was soluble in ether, alcohol and ethyl acetate but difficultly soluble in benzene, chloroform and petroleum ether. The substance was acidic and readily soluble in alkali, from which the original acid could be recovered by acidification. The test for aldehydic substance with Schiff's reagent and Tollens' solution proved negative. The substance melted at 178–180° when precipitated in prismatic needles from ethereal solution by addition of light petroleum. The melting point after purifications by sublimation at 115–120° under 5 mm. could be raised up to 184–186° (with decomp.).

The substance did not decolourise bromine or permanganate in cold showing the saturated nature of the substance. The acid was found to be dibasic by the electrolytic

conductivity method. The difference of the equivalent conductivities of N/32 and N/1024 sodium salt solutions was found 10×2.21. From the value 2.21 the substance under investigation must be dibasic. Acid value 844.3 (0.0810 g. of the sample required 39.08 c.c. of N/32 NaOH), calculated for $C_5H_8O_4$ 848.4. (Found: C, 45.53; H, 6.09. Calculated for $C_5H_8O_4$: C, 45.45; H, 6.06%. Analysis of the silver salt: Ag, 62.37. Calculated for $C_5H_6O_4Ag_2$ 62.42%.)

From the composition of the silver salt the molecular weight and the molecular formula of the acid were determined: molecular weight, 132.9; molecular formula, $C_5H_8O_4$.

We find among dibasic acids of the formula $C_5H_8O_4$, dimethylmalonic acid melting at 186° (with decomp.) whose identity with the actual substance was proved as follows.

(*a*) *Preparation of the amide.* The acid chloride prepared from 1.2 g. of the acid and 4 g. of phosphorus pentachloride was added to cold aqueous ammonia. Yellowish crystalline diamide was obtained, which after recrystallization from water furnished colourless scales melting at 262°, in good accordance with the melting point of dimethylmalonic diamide. (Found: N, 21.64. Calculated for $C_5H_{10}O_2N_2$: N, 21.54%.)

(*b*) *Conversion into isobutyric acid by elimination of carbon dioxide.* That the acid $C_5H_8O_4$ is dimethylmalonic acid was also proved by conversion into isobutyric acid by elimination of one mol of carbon dioxide from the original molecule. The acid, when heated somewhat above its melting point, loses readily one mol of carbon dioxide, the amount of which was quantitatively estimated by absorbing it in soda-lime. (Sample 2.2563 g. evolved 0.7518 g. of CO_2, calculated for $C_5H_8O_4$ 0.7521 g.) The resulted substance had the following properties: b.p. 153–153.5°/761 mm.; d_4^{20} 0.9505; n_D^{20} 1.3933; M.R. obs. 22.11, calculated for $C_4H_8O_2$ 22.21.

The substance has acidic properties and does not decolourize bromine and permanganate in cold. Acid value 636.4 (0.2033 g. of the sample required 24.32 c.c. of 0.095N NaOH), calculated for $C_4H_8O_2$ 636.3. (Found: C, 54.38; H, 9.15. Calculated for $C_4H_8O_2$: C, 54.55; H, 9.09. Analysis of the silver salt: Ag, 55.58. Calculated for $C_4H_7O_2Ag$: Ag, 55.31%.) The substance was proved to be identical with isobutyric acid by preparing its acid chloride and amide.

Isobutyryl chloride. A mixture of 1 g. of the acid and 1 g. of phosphorus trichloride was heated to gentle boiling for a few minutes. The acid chloride obtained showed the following properties: b.p. 90–93°; d_4^{20} 1.1079; n_D^{20} 1.4081. These constants are in good accordance with those of isobutyryl chloride (b.p. 92°; d_4^{20} 1.0174; n_D^{20} 1.40789) reported by Brühl[35].

Isobutyryl amide. The acid chloride was added drop by drop to well-cooled aqueous ammonia, when colourless glistening leaflets were obtained. It melted at 116–123° without purification, which was separated into two portions, namely, prismatic needles melting at 170–173° (separated at first) and glistening scaly crystals melting at 124–128°, by recrystallization from water. The substance melting at 170–173° might have been crude diisobutyryl amide, a by-product obtained by Hoffmann[36] in this reaction, but owing to the scarcity of the substance its confirmation could not be attained. The substance melting at 124–128° was once more recrystallized

(35) Brühl, *Ann.*, **203** (1880), 20.
(36) Hoffmann, *Ber.*, **15** (1882), 981.

from benzene, when it melted at 127–128° alone and in admixture with a specimen of isobutyryl amide.

(2) *Liquid portion.* The amount of liquid portion obtained after removal of dimethylmalonic acid was nearly the same with that of the latter. It showed acidic characteristics as well as those of aldehyde. The substance decolourized bromine in cold showing the unsaturated nature, and on oxidation with 4% potassium permanganate another crop of dimethylmalonic acid was obtained.

10 g. of the liquid substance was dissolved in 500 c.c. of 4% sodium bicarbonate solution and dilute permanganate solution (4%) was added drop by drop with stirring till the solution acquired permanent reddish colour, left over night at the ordinary temperature and manganese dioxide precipitated was filtered off. The filtrate after being saturated with carbon dioxide was evaporated to dryness, acidified by dilute hydrochloric acid and the oily substance thus set free was extracted with ether. The residue after removal of the solvent crystallized to a soft mass, from which a crystalline substance was separated by filtration. It proved to be dimethylmalonic acid. The liquid portion was then treated with a mixture of ether and light petroleum ether (1:1) in which dimethylmalonic acid was insoluble, and thus could be separated from the liquid portion. The filtered crystals were purified by reprecipitation from ethereal solution by adding light petroleum ether when it exhibited every characteristic property of dimethylmalonic acid.

Identification of formic acid. The ether–petroleum ether solution obtained above was then shaken vigorously with water for an hour in order to separate water-soluble acids. The aqueous layer was separated, neutralized with dilute ammonia and evaporated to smaller volume. The neutral solution produced an irritating odour on acidification with 5N sulphuric acid, while a quantity of the silver salt was precipitated on adding silver nitrate solution which immediately turned into bright grayish colour. It precipitates calomel from mercuric chloride solution. From these results it follows that the liquid portion contained formic acid.

II. Preparation of hydrocarbon from shonanic acid. (1) *By Rosenmund and Zetzche's method*[37] ($R{\cdot}COOH \rightarrow R{\cdot}CO{\cdot}Cl \rightarrow R{\cdot}CHO \rightarrow R{\cdot}CH_3$). By applying this method to the reduction of shonanic acid, the yield of aldehyde was very poor and almost all of the reaction product was a resinous matter, so that only the properties and the derivatives of the aldehyde were studied.

When shonanic acid chloride (freshly prepared) in benzene solution was treated with hydrogen in presence of palladium on barium sulphate as catalyser, the vigorous evolution of hydrochloric acid gas was observed. After the evolution of HCl gas was over, the reaction mixture was filtered from the catalyser and the yellowish matter which remained after removal of the solvent was distilled under reduced pressure. Most of the substance remained undistilled even on heating to 280° under 3 mm., and only a few drops of colourless mobile liquid (0.3 g.) of the following properties was obtained. B.p. 73°/5 mm.; d_4^{20} 0.935; n_D^{20} 1.4630; M.R. obs. 46.78, calculated for $C_{10}H_{18}O$ 46.50.

The substance showed aldehydic nature on testing with Schiff's reagent and Tollens' solution and gave a crystalline semicarbazone.

(37) *Ber.*, **51** (1918), 585, 594.

Semicarbazone. The semicarbazone was prepared from 0.22 g. of the sample, 0.14 g. of sodium bicarbonate and 0.15 g. of semicarbazide hydrochloride. Recrystallization from ethyl alcohol furnished a colourless scales melting at 165°. (Found: N, 20.03. Calculated for $C_{11}H_{21}ON_3$: N, 19.9%.) Thus it is clear that the substance obtained was the aldehyde corresponding to tetrahydroshonanic acid ($C_{10}H_{18}O_2$).

(2) *Preparation of hydrocarbon from shonanic acid by reduction with hydroiodic acid.* 5 g. of shonanic acid was heated with 10 g. of hydroiodic acid (d = 1.7) together with 1.6 g. of red phosphorus in a sealed tube as in the case of reduction of succinic,[38] palmitic[39] and hexahydro-*m*-xylic acid[40] for 5 hours at 220–225°, then another 4 hours at 240° with the further addition of 0.5 g. of red phosphorus, then 4 hours more at 250–270° with a third addition of 0.5 g. of red phosphorus and 0.7 c.c. of water. The contents of the sealed tube were then poured into 200 c.c. of water, shaken with 5% sodium hydroxide solution to remove acidic substance, dried over anhydrous sodium sulphate and then ether was distilled off. The light mobile oil remaining behind was rectified twice under the ordinary pressure over metallic sodium and in this manner a hydrocarbon of the following properties was obtained. (Yield 1.3 g.) B.p. 157–158.5°/754 mm.; d_4^{20} 0.7866; n_D^{20} 1.4344; M.R. obs. 46.37, calculated for $C_{10}H_{20}$ 46.18. The substance does not decolourize either bromine or permanganate showing that the substance is saturated. (Found: C, 85.62; H, 14.37; molecular weight in phenol, 144.7. Calculated for $C_{10}H_{20}$: C, 85.7; H, 14.3%; molecular weight, 140.2.)

(3) *Preparation of hydrocarbon from tetrahydroshonanic acid by reduction with hydroiodic acid.* Next, exactly the same method as in the case of (2) was applied to tetrahydroshonanic acid taking 16 g. of the acid and the product showed the following properties: b.p. 158.5°/765 mm.; d_4^{20} 0.7872; n_D^{20} 1.4338; M.R. obs. 46.34, calculated for $C_{10}H_{20}$ 46.18. Inert against bromine and permanganate. (Found: C, 85.49; H, 14.36. Calculated for $C_{10}H_{20}$: C, 85.7; H, 14.3%.)

(4) *Preparation of hydrocarbon C_9H_{16} F_1 by the dry distillation of tetrahydroshonanic acid with soda-lime.* Tetrahydroshonanic acid (10 g.) was heated with soda-lime (30 g.) under ordinary pressure. A little oily matter began to distil over at 134° which ceased at 150°. Yield 6.0 c.c. It was fractionally distilled over metallic sodium and was separated into three portions as shown in Table 3. The fraction (3) was again subjected to another fractional distillation under ordinary pressure and the following fractions were obtained (Table 4).

Table 3.

Fr. No.	B.p./763 mm.	Vol. (c.c.)
1	75–138°	0.8
2	138–141°	1.0
3	141–149°	3.8

Table 4.

Fr. No.	B.p./755 mm.	Vol. (c.c.)
a	142–145°	0.4
b	145–148°	3.1
c	148–149°	0.2

(38) Berthelot, *Ann.*, **147** (1868), 376.
(39) Kraft, *Ber.*, **15** (1882), 1689, 1711.
(40) Aschan, *Ber.*, **24** (1891), 2718.

The main fraction b was once more rectified and 2.7 g. of hydrocarbon with the following properties was obtained. B.p. 144.5–145°/757 mm.; d_4^{19} 0.8129; n_D^{19} 1.4595; M.R. obs. 41.12, calculated for C_9H_{16} ⊏ 41.07. The hydrocarbon obtained absorbs bromine readily and decolourizes permanganate in cold. Bromine value 1236 (0.2403 g. absorbed 0.297 g. bromine), calculated for C_9H_{16} ⊏ 1290. (Found: C, 86.95; H, 12.60. Calculated for C_9H_{16}: C, 87.1; H, 12.90%.) The attempt to obtain its nitrosochloride or nitrosite in the crystalline state was not successful.

III. Preparation of *o*-dinitrobenzene from shonanic acid. 5 g. of shonanic acid was heated on the water-bath with 50 c.c. of nitric acid (d = 1.12) with constant stirring. A brisk reaction took place at first, which soon subsided but the heating was continued for 5 hours. On standing over night long needle crystals appeared, which were filtered off and recrystallized from water. It melted at 117–118°. The filtrate bore an odour reminding of nitrobenzene and on evaporating another crop of crystals was obtained, which proved to be the same substance as the main product. The substance was neutral and the presence of nitrogen was recognized by the evolution of ammonia on heating with soda-lime. (Found: C, 42.75; H, 2.38; N, 16.67. Calculated for $C_6H_4O_4N_2$: C, 42.86; H, 2.38; N, 16.67%.)

The empirical formula of the substance calculated from the experimental data is $C_3H_2O_2N$ while among the substances corresponding to this empirical formula *o*-dinitrobenzene melts at 117.5°. The substance showed no depression of the melting point in admixture with *o*-dinitrobenzene, thus the identity of these two substances being proved.

Summary.

(1) Dimethylmalonic acid and formic acid were obtained by the oxidation of shonanic acid.

(2) A hydrocarbon $C_{10}H_{20}$ was obtained by the reduction of shonanic and tetrahydroshonanic acid with hydroiodic acid.

(3) A hydrocarbon C_9H_{16} ⊏ was obtained by the dry distillation of shonanic acid with soda-lime.

(4) The attempt to determine the ring structure of shonanic acid by comparing the properties of these hydrocarbons with those of known hydrocarbons gave no reliable results.

(5) The formation of *o*-dinitrobenzene from shonanic acid by treating it with dilute nitric acid may be taken as an evidence for the presence of six-membered ring system in its molecule.

In conclusion, the author wishes to thank Prof. K. Kafuku for his kind advices and suggestions rendered during the course of this work.

Department of Industry,
Government Research Institute of Taiwan.